

RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues (\$2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of \$4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and Libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of \$6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman.....E. R. BRIDGWATER, E. I. du Pont de Nemours and Company
Vice-Chairman.....L. B. SEBRELL, Goodyear Tire and Rubber Company
Secretary-Treasurer.....H. E. SIMMONS, University of Akron, Akron, Ohio
Executive Committee..H. A. WINKELMANN, W. N. JONES, N. A. SHEPARD, H. R. THIES, S. M. CADWELL
Sergeant-at-Arms.....E. H. NAHM

The Fall Meeting of the Rubber Division of the American Chemical Society in Denver, August 23-24, 1932

The meeting was held in the Shirley Savoy Hotel with fifty-five in attendance at the opening session. The Chairman appointed a Nominating Committee consisting of W. W. Vogt, Fred Amon, and W. R. Hucks.

The following papers were then presented by their authors:

August 23, Morning Session

10:00-10:20 H. L. Wiley. Rubber Pigment Ratios in Batch Control.
10:20-10:30 Discussion.
10:30-10:50 J. H. Fielding. Slide Rule Calculation of Time-Temperature Relations in Vulcanization.
10:50-11:00 Discussion.
11:00-11:20 G. S. Haslam. The Effect of Particle Size on the Physical Properties of Rubber.
11:20-11:30 Discussion.
11:30-11:50 W. C. Mathews and G. S. Haslam. Some Factors Involved in the Banbury Mixing of Zinc Oxide.
11:50-12:00 Discussion.

August 24, Morning Session

10:00-10:20 R. V. Sandstrom. Determination of the Temperature Coefficient of Vulcanization. II.
10:20-10:30 Discussion.
10:30-10:50 G. K. Hinshaw. Evaluation of Variable Temperature Cures.
10:50-11:00 Discussion.
11:00-11:20 Ira Williams and H. W. Walker. The Effect of Oxygen and Water on the Polymerization of Chloroprene.
11:20-11:30 Discussion.
11:30-11:50 E. H. Krismann and E. R. Bridgwater. Some Factors Affecting the Rate of Vulcanization of Chloroprene Plastic Polymers.
11:50-12:00 Discussion.
12:00. Business meeting.

At the business session held on August 24, W. W. Vogt reported for the Nomi-

nating Committee as follows: *Chairman*, L. B. Sebrell; *Vice-Chairman*, E. P. Curtis, Ira Williams; *Secretary-Treasurer*, H. E. Simmons; *Executive Committee*, F. W. Stavely, A. F. Pond, L. J. D. Healey, A. C. Eide, L. C. Peterson, Harold Gray; *Sergeant-at-Arms*, C. C. Christensen, Gladding Price.

By motion the report of the Nominating Committee was received and voted to close the nominations. It was also decided by motion that the election of officers for the Division for the following year should be carried out by mail, and the Secretary was instructed to prepare the ballots.

The Secretary's report and also that of the Treasurer were read and by motion accepted, which reports are as follows:

Secretary's Report

Total Membership of the Division.....	632
Members.....	453
Associate members.....	96
Subscribers.....	83
	<hr/>
	632
Honorary members 31 (not included in the above total)	

(NOTE: By motion of the Executive Committee the Secretary was instructed to inform the Honorary Members of the Rubber Division that in the future if they wished to received RUBBER CHEMISTRY AND TECHNOLOGY it would be necessary for them to pay \$4.00 per year.)

Treasurer's Report

Balance in bank at Detroit meeting (April).....	\$1508.04
Received as surplus from the Rubber Division dinner in Detroit.....	361.90
Received from dues and subscriptions.....	427.31
	<hr/>
Total Receipts.....	\$2297.25
Disbursements:	
Expenses of Secretary to Detroit.....	\$35.98
Printing letter for fall meeting, return cards and envelopes.....	63.00
Postage, office supplies, telephone calls and tele- grams.....	13.95
Identification badges for Detroit meeting.....	7.05
Stenographic services (6 months).....	60.00
Collection on foreign checks.....	1.25
	<hr/>
	181.23
Balance in bank August 18, 1932.....	<hr/>
	\$2116.02

By motion the Division expressed its appreciation to C. C. Davis for the fine work which he is doing in the editing of RUBBER CHEMISTRY AND TECHNOLOGY.

A vote of thanks was extended our retiring Chairman, E. R. Bridgwater, for the success in securing advertising for RUBBER CHEMISTRY AND TECHNOLOGY.

H. E. SIMMONS, *Secretary-Treasurer*

Denver Meeting

The Denver meeting surpassed even the expectations of those who were most optimistic in regard to the number who might attend and also the program of the Division.

The Division had fifty-five registered chemists in its meetings, and the discussions of the various papers were more valuable than usual because of ample time.

The Division dinner was a great success, consisting of an auto trip up to Mount Evans and then a steak and corn roast in Genessee Park.

After the roast we were entertained by the Cow Boy quartette who broadcast over RKO.

This wonderful outing and entertainment was made possible through the courtesy of the Gates Rubber Company. The Rubber Division wishes to express a vote of thanks to the company and also the individuals in the company who contributed to the pleasure of us all.

Los Angeles Group Meeting

June 7, 1932. Address by W. R. Hucks (Pacific Goodrich Company) on "Recent Applications of Liquid Latex." New Vice-Chairman, Paul Beebe.

Recommended Standard Practice for the Geer-Oven and Oxygen-Bomb Aging of Rubber Stocks

Physical Testing Committee, Rubber Division American Chemical Society

I. General Specifications, Applicable to Both Types of Aging

1. One large unit or a number of small ones is equally satisfactory.
2. The means of heating the apparatus is optional.
3. The operating temperature shall be 70° C. in both cases.
4. The allowable temperature variation shall be $\pm 1^\circ$ C.
5. A record of the temperature should be made, preferably with a recording thermometer. The situation of the bulb is specified for both cases.
6. Stocks for aging shall be in the form of A. C. S. standard physical test sheets (cf. *Rubber Age* (N. Y.), January 25, 1930) when tests of tensile strength or modulus are to be made subsequent to aging. Otherwise any convenient form may be used. For bomb aging, where the regular sized sheets are too large to be conveniently handled, they should be cut into strips 1 1/4" wide and handled in the regular manner.
7. At least 3 test strips (available from one sheet) of each cure shall be aged.
8. The samples shall be individually spaced and shall hang free in the aging chamber.
9. Where buffing is required, samples shall be buffed before aging.
10. The removal of a copper conductor from the insulation in testing a sample of wire or cable is optional, depending on the size of the conductor.
11. Test strips shall be gaged for tensile test after aging.

12. Samples shall be held a minimum of 16 hours at test-room conditions from the time of their removal from the aging chamber until the time of making physical tests.

13. Different intervals of aging shall be tested individually as they occur in the progress of the age-tests, disregarding the fact that more stock is still aging.

14. The extent of deterioration shall be judged by the decrease in tensile strength, ultimate elongation, stress-strain properties, flexibility, hand tear, and the change in appearance.

II. Geer-Oven Aging

1. Dimensions of Oven—Minimum, 12 x 12 x 12 in. Maximum, 36 x 36 x 48 in.

2. The make of oven is not restricted.

3. The heating elements shall be situated in the air-supply outside the aging chamber proper.

4. Temperature control shall be automatic, the controlling bulb or thermostat being situated at the top center of the aging chamber.

5. The bulb of the thermometer, recording or otherwise, shall likewise be situated at the top-center of the aging chamber.

6. The actual allowable temperature difference between various parts of the aging chamber shall be 2° C. from the operating temperature.

7. The circulated air shall be changed—not just agitated—fresh air being introduced at room temperature.

8. Care should be exercised that the circulating air is at no time in contact with the fan motor brush discharge.

9. A stationary support for the samples is acceptable, but a moving one is recommended.

10. The standard aging periods shall be 2, 4, 7, 14 days or more, depending on the requirements.

III. Oxygen-Bomb Aging

1. The heating medium shall be water.

2. The situation of the heating units is optional.

3. The temperature control shall be automatic, the controlling bulb or thermostat being situated in the heating medium.

4. The heating medium shall be in a constant state of circulation, the change being rapid and complete.

5. The temperature of the bomb shall be considered as that of the heating medium.

6. The aging is to be started with a bomb which is up to temperature.

7. The operating pressure shall be 300 lb. per sq. in. and shall be maintained through an automatic pressure regulator, in open connection with the oxygen supply.

8. The separation of stocks as to type for aging together is optional, but it is recommended that the control be aged with all special or experimental stocks, regardless of type.

9. The standard aging periods shall be multiples of 24 hours as required.

August 19, 1932

New Books and Other Publications

Special Survey of the Rubber Goods Industry. R. G. Dun & Co., New York, N. Y.

This broadside from "Dun's Review" is a comprehensive survey compiled from information reported by offices and correspondents of R. G. Dun & Co., located in the principal producing and distributing centers in the United States. Crude rubber production and the attempts to curtail it are reviewed, and the statistical relation of production and consumption is tabulated, also the record of rubber prices showing their decline to the present low record. Tire production, quality, and decline in shipments are discussed. In footwear the decline of stocks is noted. Yearly production of proofed fabrics, heels, and soles is reported from 1925 to 1931, inclusive. The current conditions of rubber goods distribution are outlined as reported from 16 cities from coast to coast in the United States. [From *India Rubber World*.]

National Directory of Commodity Specifications. Classified and alphabetical lists and brief descriptions of specifications of national recognition. Miscellaneous Publication No. 130. Prepared by Clarence W. Ingels under the direction of A. S. McAllister, Chief of the Division of Specifications, United States Government Printing Office, Washington, D. C., 1932. Cloth, 548 pp., 7½ by 11 inches. Indexed.

This volume is an attempt on the part of the Department of Commerce to collect and publish a classified list and brief description of the standards and specifications formulated by the national technical societies, the trade associations having national recognition, or other organizations which speak for industry or with the authority of the Federal Government as a whole.

The standards and specifications for rubber products mentioned in the directory are too numerous to list, there being, for example, specifications for no less than 16 different kinds of hose alone, and for 11 different kinds of druggists' rubber sundries, these having been prepared by various national technical societies, trade associations, and the Federal Specifications Board. [From *India Rubber World*.]

Yearbook of Agriculture, 1932. Milton S. Eisenhower, Editor, Arthur P. Chew, Associate Editor. United States Government Printing Office, Washington, D. C., 1932.

This yearbook of the United States Department of Agriculture contains, in addition to the general report of the year in agriculture by the Secretary of the Department, a series of articles by specialists and voluminous statistical information of agricultural and trade interest, including imports of crude rubber and international rubber trade. There is also a brief article on "Rubber Plant Hybrids of Madagascar Species," that proved vigorous in the United States. [From *India Rubber World*.]

Rubber Information. Published by Leonard Hill, Ltd., London, 1932. Second Edition. 144 pp. 10 shillings.

This is the second edition of what might be termed the British handbook of the rubber industry. It is a compendium of the British industry in all its phases, including plantation and factory practices, British rubber chemicals and chemical houses, trade statistics, rubber machinery and equipment, British rubber manufacturers and a guide to British rubber trade-marks. The edition shows a distinct improvement over the previous volume. [From *The Rubber Age* of New York.]

Use of Rubber Latex in the Shoe Trade. Issued by the Rubber Growers Association, London. 1932. 12 pp. For free distribution.

The brochure is a comprehensive review of the latest developments in the application of latex in the shoe making industry. The increasing use of latex makes this subject of special importance. The book is well illustrated and details the operations in use today in the utilization of latex in footwear. It also carries directions as to the handling of latex. [From *The Rubber Age of New York.*]

Zinc Oxide Incorporation in the Banbury Mixer. Published by the New Jersey Zinc Company in conjunction with the Farrel-Birmingham Company. 1932. 12 pp. For free distribution.

Much attention has been given to the dispersion of zinc oxide in rubber in the Banbury mixer and, with the coöperation of Farrel-Birmingham Company and several rubber manufacturers, there has been gathered together available information in handy form in this booklet.

To obtain uniformly satisfactory results considerable attention to procedure is necessary. The booklet deals with such matters as the temperature at which the mixing operation is carried out, the rate of addition of zinc oxide, and the preparation of the rubber prior to mixing the master batches. [From *The Rubber Age of New York.*]

The Vanderbilt 1932 Rubber Handbook. W. F. Russell, Editor. R. T. Vanderbilt Co., Inc., 230 Park Ave., New York, N. Y. Flexible covers, 174 pp., 4 by 7 inches. Indexed.

This new edition of nearly 200 pages promises to be even more useful to the rubber technologist than its predecessor. The colored loose-leaf pages divide the volume into 3 distinct sections. The first gives a complete description of each of the Vanderbilt products with extensive data for their successful use in rubber compounding. Many references are made to the more extensive experiments recorded in *The Vanderbilt News*. The clearness and conciseness with which this material is presented is salesmanship of the highest order.

The second portion consists of a series of authoritative articles on the more scientific side of rubber. The material is contributed by 29 specialists in their respective fields. The editor is to be congratulated for securing chapters from Europe as well as from this country, thereby adding to the prestige of the collection. Many of the subject titles have been retained from the previous edition, but the reviews have been completely rewritten. The subject matter of the new chapters reflects the trend of scientific and technical developments in the industry. The topics treated range from the more lowly problems, such as sulfur analysis, to the purely scientific question of the x-ray investigation of the hydrocarbon. An excellent summary of the theories of vulcanization is included.

The third section contains data and tables for the every-day use of the rubber compounder. The material on volume costs, specific gravity, methods of computation, etc., allow the compounder to design and calculate the characteristics of his rubber compounds in an easy and efficient manner.

The handbook cleverly combines the advertising of compounding materials from a thoroughly scientific viewpoint with material that summarizes much of our present knowledge of rubber. This and the reference tables assure that the manual will be in constant use by its possessors. Reviewed by C. R. Boggs. [From *India Rubber World.*]

Colloid Chemistry, Theoretical and Applied. By Selected International

Contributors, Collected and Edited by Jerome Alexander. Vol. IV. Second Series of Papers on Technical Applications. The Chemical Catalog Co., Inc., 419 Fourth Ave., New York, N. Y., 1932. Cloth, 734 pp., 6 by 9 inches. Illustrated. Indexed. Price \$11.50.

The series of which this book is the concluding volume has been justly designated as the most comprehensive and modern treatment of colloid chemistry in any language. The scope of this volume embraces comprehensive articles in the following industrial fields: carbohydrates, including cellulose, wood, paper, explosives, sugar, starch products, sizing, dyeing, rubber, plastics, tanning, photography, coatings, including paints, color lakes, and electro-deposition, foods, laundry and dry cleaning, solidified alcohol, and fire extinguishers, water supply and sewage disposal.

The section devoted to rubber comprises 4 chapters as follows: Latex and Its Industrial Applications by A. Van Rossem; Structure of Rubber by E. B. Spear; Physico-Chemical Aspects of Hevea Rubber by R. P. Dinsmore; and Carbon Black in Rubber by N. A. Shepard. In these chapters the authors present the facts and theories thus far revealed by researches and technical processes on the chemical and physical constitution of rubber and its properties. Each chapter is supplemented by an extensive bibliography for further guiding the interested student to the original sources.

The series of 4 volumes is a work of great magnitude and high practical value to chemists and students in many branches of science and technology. [From *India Rubber World*.]

Annual Survey of American Chemistry. Vol. VI. Calendar Year 1931. Edited by Clarence J. West. Foreword by Henry K. Benson, Chairman, Division of Chemistry and Chemical Technology. Published for National Research Council by The Chemical Catalog Co., Inc., 419 Fourth Ave., New York, N. Y., 1932. Cloth, 573 pp., 5 by 8 $\frac{1}{4}$ inches. Author and subject indices. Price, \$4.50 net.

In this volume a full review of rubber research for 1931 is given by John T. Blake, research chemist, Simplex Wire & Cable Co., Boston, Mass. The topics covered are American rubber, synthetic rubber, chemistry and structure, vulcanizing agents, accelerators, oxidation and antioxidants, scorching and antiscorchers, compounding and compounding ingredients, testing and analysis, latex, electrical insulation, and practical applications. [From *India Rubber World*.]



Rubber Latex

Recent Scientific and Technical Developments

V. N. MORRIS AND H. W. GREENUP

Firestone Tire & Rubber Co., Akron, Ohio

The more or less scientific work which has been carried out on the rubber plantations, and the problems relating to the production of articles from latex in the factories of America and Europe are discussed. A review is given of the actual and proposed uses for latex and products made from latex.

TEN years ago, latex, the white liquid obtained from the rubber tree, was as much a stranger to manufacturers in Europe and America as it is to the public today. At the Fifth International Rubber Exhibition in London, in 1921, latex is said to have been gazed upon as a curiosity even by scientists connected with rubber-manufacturing concerns. In the past decade, however, the direct utilization of this liquid in rubber and other industries has had such a rapid advance that 9,190,362 pounds of rubber, in the form of latex, were imported into the United States in the first ten months of 1931. It is significant to note that the importation of latex was 19.3 per cent greater in 1930 than in 1929, despite the fact that the consumption of crude rubber decreased 20 per cent (16).

The opportunity for revolutionizing a major industry does not often occur. Given the proper economic conditions, it is not outside the realm of possibility that the direct use of latex could accomplish such a revolution in the rubber industry. The earliest manufacturers of rubber articles (the natives of the Amazon district) used latex as their raw material. The difficulty formerly encountered in the transportation of

latex without coagulation and the necessity for transporting so much water, combined to retard interest in its direct application in the more industrialized countries. The rubber in a modern manufactured article has usually, therefore, been collected at the tree in the form of latex, coagulated with formic or acetic acid, washed, sheeted, dried and smoked, packed, shipped to this country, unpacked, plasticized by mechanical working in heavy machinery, compounded by the mechanical introduction of the desired ingredients, and vulcanized in a mold of suitable shape. The history of the rubber in an article manufactured from latex, on the other hand, is that of collection of the latex; shipment to this country in the presence of a preservative; compounding by stirring the ingredients into the liquid latex in the presence of suitable protective agents; forming by dipping, deposition, or other methods; and finally drying and vulcanizing. The simplicity of the latter procedure as compared with the former is obvious.

Simplicity in manufacture is by no means the only advantage claimed for products made from latex. Investigators in the field are generally agreed that latex products, if properly made, are superior in physical properties, since no mechanical deterioration of the rubber occurs as a consequence of milling. Further advantages claimed for latex products include great saving in power consumption in the mixing procedure, greater uniformity in product, better dispersion of compounding ingredients, better aging, lower accelerator costs, and elimination of fire and health hazards in processes formerly requiring rubber cements (made with toxic and inflammable solvents).

It is true that all of the advantages claimed have not been accepted without dispute. The writers have found, for instance, that, despite the supposed presence of naturally occurring antioxidants, products made from preserved latex do not always withstand aging well (particularly if the latex remains in the unvulcanized state). Furthermore, in order to obtain the high resistance-to-tear desired of certain latex products it usually seems necessary to maintain a somewhat "undercured" state, which results in high permeability and high permanent set. The present extraordinarily low price of crude rubber also places latex (with its high cost of transportation) at a disadvantage.

Great as has been the commercial adoption of latex in recent years, the increase in the literature pertaining to latex seems to have been even greater. The direct utilization of this material so appeals to the imagination that it has stimulated both inventive and literary effort. The literature has been increasing at such a rate, in fact, that even in 1924 van Rossem (126) considered it inadvisable to attempt to review it all in one paper. Early in 1927 Hauser published his book on the subject of Latex (71). In view of the adequate manner in which this book covers developments prior to that time, the

present article has been confined very largely to the scientific and technical developments of the past five years. Since the writers have listed hundreds of references to patents and journal articles pertaining to latex which have appeared in this period (about two hundred in 1930 alone), no attempt has been made to cover every reference in this review. Only those which seem to be of most interest have been discussed. Although some investigations of a strictly scientific nature have been reviewed, emphasis has been placed on the developments having possible practical application.

SCIENTIFIC INVESTIGATIONS OF LATEX SYSTEMS

INFLUENCE OF ANATOMY OF TREES ON YIELD OF LATEX. A means of predicting the future yield of young *Hevea* trees has been the object of many researches. Such a method would avoid the planting of poor yielding trees, or would enable them to be detected and replaced before the tapping age was reached. For this reason the method suggested by Ashplant (17) has created widespread interest. It depends upon the determination of the bore of the latex tubes and the number of latex rings. Trees with latex tube bores below a certain average are said to be poor yielders, and good yielding trees are said to possess latex tubes above average bore. Whether or not a tree with large tube bore is a good yielder depends on the number of latex rings. Some workers have failed to confirm Ashplant's results. With respect to the data of Frey-Wyssling (63), Ashplant has claimed that they support (as far as they go) his results, but that too few trees and trees of too restricted tube bore were studied. Ashplant makes the statement that this method has been of value in rejecting poor trees and was preferable at the time of its introduction to the indiscriminate planting then taking place.

Eaton and Fullerton (57) have reported that a greater dry rubber content is obtained by shallow tapping than by deep tapping, while Sanderson and Sutcliffe (128) have established correlations between the girth of the tree, number of latex rows at 20 inches above the ground, cortex thickness, and the yield of latex. They were also able to correlate the yield of one year with that of another.

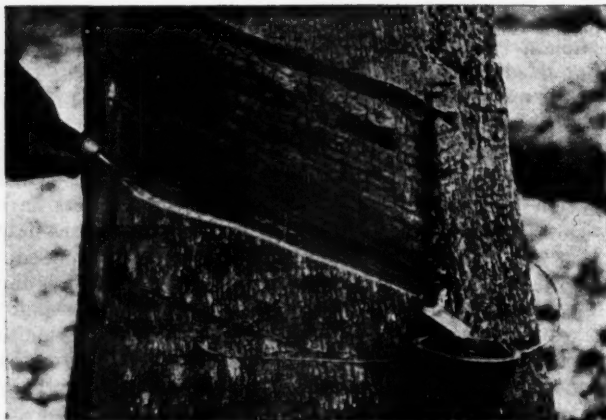
Another method of predicting the yield, which is advocated by Hauser (70), and applies to grafted trees, consists of determining the shape of the particles in the latex. If the shapes of the particles in the latex from grafted stock are the same as those of the particles in the latex from the mother tree, the graft is usually successful from the standpoint of latex yield.

STRUCTURE OF LATEX PARTICLE. The structure of the latex particle is still the subject of considerable dispute. Hauser's theory of the two-phase structure of latex has been subjected to criticism, especially by von Weimarn (163a). The latter considers latex a polydisperse system of isoaggregated particles (isospherulites), the general consistency of

which is fluid-gelatinous. He also believes that the serum constituents are present not only in the surface film but also on the inside of the latex particle, and play an important role in the changes the isoaggregates undergo during the drying and other coagulating processes.

Von Weimarn disagrees with Hauser in finding many spherical or near-spherical particles, and has reported that in certain cases some of the particles flow together. This was especially true when the temperature was raised to 100° C. or when the protein film was removed with a "dispergator" such as lithium iodide.

Hauser (73) repeated his previous experiments on the dissection of the latex particle, using an improved apparatus (Leitz dark ground illuminator), and confirmed the previously described structure. He reported that the interior of the particle is fluid but gels when the particle is coagulated or



Courtesy of Revertex Corp. of America

FIGURE 1. TAPPING A HEVEA TREE WITH A QUARTER CUT

dried or when it is punctured. The consistency of the fluid interior varies with the age of the tree, being even gelatinous in the case of very old trees. (See Figure 2.)

METHODS OF MEASURING pH IN LATEX. The measurement of the hydrogen-ion concentration of latex has been an important problem and one which has proved difficult to solve. The Wulff colorimetric foil method, recommended by Hauser, has been stated by MacKay (102) to be unreliable in certain ranges. The diffusion of indicator outward from the gelatin foil is another objectionable feature. The use of the glass electrode in latex has been described by McGavack and Rumbold (110) who found it to be sufficiently accurate over the range investigated (pH 8 to pH 12). Van Harpen (69) has used the quinhydrone method in a thorough study of the hydrogen-ion concentration of fresh latex and the adsorption of hydrogen ions by the latex particles.

SURFACE TENSION OF LATEX. Hauser and Scholz (76) have determined the surface tension of different lattices and have found values of 40.5 dynes per centimeter for fresh, and of 35.5 for ammonia-preserved latex. They also found that the surface tension passed through a minimum upon dilution with water, as do surface tensions of potassium soap solutions. Scholz (132) later found the surface tension of fresh latex to vary inversely with the percentage of nonrubber constituents in the serum. He also observed that the surface-active substances remained in the serum upon coagulation.

NONRUBBER CONSTITUENTS IN LATEX. Though the non-rubber constituents in latex have received considerable attention in the past few years, not until very recently had any extensive series of determinations of these constituents been reported in the literature. From the results of several hundred determinations, Scholz and Klotz (134) conclude that in fresh normal lattices of varying rubber content (from 35.2 to 49.4 per cent) the variation in nonrubber constituents is only from 3.0 to 2.6 per cent; and for that important class of lattices of rubber content between 37 and 43 per cent, the non-rubber content is 2.9 per cent.

Although the value of these materials was formerly much disputed, the rather extensive investigations of Martin (105) appear to have proved definitely that some material in the serum remaining after coagulation is capable of improving the aging properties of rubber to a marked extent. This investigator reported, for instance, that a crepe rubber-sulfur mix, to which had been added 3 per cent of dried serum, suffered no loss in tensile strength after 6 days in the Geer oven at 70° C., whereas a similar mix containing no serum had its tensile strength reduced from 1950 to 750 pounds per square inch.

Interest in the antioxidizing power of dried latex serum has not been confined to the Far East. Patents for the use of this material as a compounding ingredient in rubber have been issued both to Italian and to English interests (140). In regard to investigations along this line in America, Hopkinson (82) states that the substance which improves the aging property of sprayed rubber has been isolated in the laboratory. He reports that it is an antioxidant, "one form of which we are now preparing and using to improve the aging of products not containing sprayed rubber."

The nonrubber constituents of latex possess accelerating as well as antioxidizing power. Thus Hopkinson states that an accelerator of excellent properties is naturally present in the latex. Rubberstocks containing this accelerator are said to have a very flat curing curve and not to be prone to overvulcanizing or to burning on the mill. The more rapid curing characteristics of sprayed latex rubber are attributed to this natural accelerator. Some work carried out in Malaya on the isolation and study of various ingredients in the serum is of interest in this connection. Eaton, Rhodes, and Bishop (58) extracted

a lipin from latex and found it to have noticeable accelerating power.

Another ingredient of the serum to be given recent attention is quebrachitol, the monomethyl ether of hexahydroxycyclohexane. McGavack and Binmore (109) and Levi (99) have proposed methods of recovering this material. In discussing the possible uses of this compound, McGavack and Binmore state that it may serve as a substitute for saccharin or as a raw material for the manufacture of quinones, photographic developers, or therapeutic chemicals.

The studies made on the resins, yellow pigment, etc., in latex are also worthy of mention. Frey-Wyssling (62) has reported some interesting microscopic investigations. Among other things, he found that the resins occur in the form of globules which are perfect spheres and which are generally larger than the caoutchouc particles. These resins account for the yellow or red color of latex from new tappings. Having a higher specific gravity than the rubber hydrocarbons, they concentrate in the serum during centrifuging.

DETERMINATION OF RUBBER CONTENT OF LATEX. The usual methods of determining rubber or total solids of latex, although sufficiently accurate, are time-consuming. For this reason the method of Ward and Gehman (162) has proved interesting. The method, which consists of determining the obscuring power of the lattices in a microturbidimeter, calibrated with lattices of known rubber content, is said to have an accuracy of 1 per cent in 35 per cent rubber latex, when dilutions of 15 per cent or less are used. The turbidity of latex is dependent upon the refractive index of the serum and the number and size of the latex particles. Fortunately the refractive indices of water and of the serums of various fresh and preserved lattices are similar, and, by the use of color filters, small variations are nullified. It remains to be seen whether the variations in particle size encountered in lattices from young and old trees affect the accuracy of the method.

Scholz and Klotz (153) have recently proposed modification of the usual method for the determination of total solids. By carefully drying the latex in a nickel dish over an open flame, they were able to obtain accurate values for dry total solids in 8 to 10 minutes.

COAGULATION OF LATEX. Among the more extensive investigations of the coagulation of latex have been those relating to the effects of hydrogen-ion concentration (176). Although latex is ordinarily coagulated by acids and stabilized with alkaline substances, there is (for lattices of suitable concentration) a second zone of complete dispersion in the acid range. According to Fullerton's recent experiments, samples of latex, diluted to a rubber content of 4 per cent, were completely coagulated at pH 0.8; partially coagulated from pH 0.8 to 1.0; completely dispersed from 1.0 to 3.5; partially coagulated from 3.5 to 3.8; completely coagulated from 3.8 to 4.83; partially coagulated again from 4.83 to

4.91; decreasingly flocculated from 4.91 to 5.30; and completely dissociated at higher pH values.

It has been so common in discussions of the production of rubber to refer to acetic acid as the coagulant that it is doubtful whether even the rubber technologists of this country and Europe realize to what extent this material has been replaced by formic acid. According to van der Burg (31), 80 per cent of the estates in the Dutch East Indies were using formic acid as early as 1927. He contends that the economy said to result from the substitution of this material for acetic acid is merely an illusion, since formic acid corrodes the mill rolls, coagulating vessels, and other utensils so much more rapidly than acetic acid. O'Brien (116) has countered with the statement that his experiments indicate that it would require fifteen years

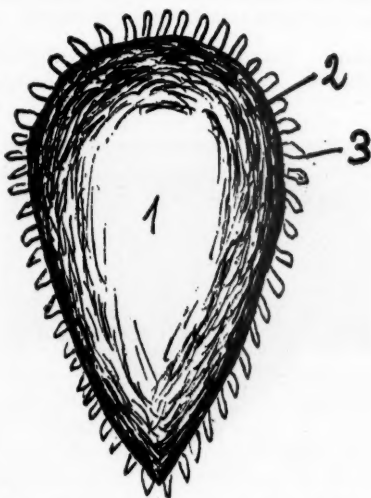


FIGURE 2. STRUCTURE OF LATEX PARTICLE (ACCORDING TO E. A. HAUSER)

1. Viscous rubber interior
2. Nearly solid elastic rubber shell
3. Adsorption layer of albumins and resins

for formic acid of twice the strength used for coagulation to corrode through a good grade of aluminum coagulating pan.

Another substitute for acetic acid which has been investigated considerably and used to some extent is sodium silicofluoride (Na_2SiF_6). Aluminum pans cannot be used with this coagulant, owing to corrosion. O'Brien (116), van Harpen (176), and others have successfully used a mixture of sodium silicofluoride with a small proportion of formic acid as coagulating agent.

Other coagulants, to which some attention has been given during the past four years, include alcohol, alum, sodium biformate, guanidines, and amines. The volume of alcohol required is too great to permit its being considered com-

mercially. The use of guanidines, such as diphenylguanidine, as coagulating agents was suggested in connection with "heat-sensitized" latex, which will be discussed later (120). Gracia (66) has proposed the use of amines (for example, allyl or benzyl) as coagulants in cases where compounding ingredients capable of reacting with acids have already been added to the latex.

There have been a number of investigations of coagulation which are of scientific interest but no great practical significance. These can be given but very brief mention in an article of this nature. They have involved, among other things, the effects of enzymes, of bacteria, and of freezing in promoting coagulation, and the role of proteins in retarding coagulation (41, 176).

PRESERVATION AND SHIPPING

PRESERVATION. Although ammonia is still the most widely used preservative for latex (9), a large number of other



FIGURE 3. RECENTLY DEVELOPED RUBBER CUP FOR COLLECTION OF LATEX

materials have been suggested (132). Sulfonic acid salts, which prevent coagulation by their protective and not germicidal action, are of especial use in latex to be applied to fabric. McGavack and Sheve have used sulfonic alkyl-aryl reaction products, with or without formaldehyde or other preservatives, while the former has found alkali salts of selenious or tellurous acids and also certain alcohols and ketones to be efficient preservatives.

Nekitin has found that certain aliphatic hydrocarbon mixtures, such as gasoline or kerosene, assist phenols in preservation. Mixtures of formaldehyde and trisodium phosphate; neutral or alkaline salts of ester acids, such as methyl sulfuric acid; and mixtures of borax and boric acid have also been suggested. It is interesting to note that alkylamines have been patented as preservatives for fresh

latex by the I. G. Farbenindustrie Akt.-Ges., and as coagulants for compounded latex by Gracia.

SHIPPING. The shipping of latex has changed remarkably in the last few years. Instead of drums or even small tinned cans, ballast tanks in steamers, or even tank ships are being used for the purpose (12).

It has been reported by the Department of Commerce that a new type of vessel has been designed. The ship is fitted with special tanks which are electrically heated so as to carry latex or coconut oil in bulk to any climate in exactly the same condition as when loaded.

Latex, concentrated by centrifuging, is being shipped to the Dunlop Company in England in the new Kenward barrels (163). These consist of two shells, fastening in the center, and are capable of being nested like beakers for the purpose of reducing the freight charges when returning them empty to the plantation.

Hopkinson (81) has described a new shipping container made from sheets of rubber. After emptying the latex, the container may then be used as ordinary rubber.

CONCENTRATION OF LATEX

Since latex contains considerable water (60 per cent or more) and must ordinarily be transported thousands of miles before it is used industrially, it is apparent that any method which allows removal of much of the water on the plantations should serve as a boon to the direct use of this material in manufacturing. The several methods for concentrating latex, which have been developed or at least investigated in recent years, are discussed under the headings of Evaporation, Centrifuging, Creaming, and Filtration.

EVAPORATION. As mentioned by Hauser (71) in his discussion of the methods of concentrating latex by evaporation, it is customary to increase the stability of latex by adding alkaline preservatives or protective colloids before or during evaporation. In a method patented by Gibbons and Shepard (65), ammonia is continually added to latex in a flat pan. A heated gas is passed over the surface, which is kept at a constant level, and a stirring device is used to prevent the formation of a surface film. In the manufacture of Revertex, a concentrated latex which has been marketed for several years, stability has been insured by introducing both potassium hydroxide and a potassium soap into the latex prior to evaporation. Several patents relating to the Revertex process (Figure 4) or the preservatives to be used therewith have appeared in the past four years (122). According to the latest patent, the potassium salts of hydrotropic substances are recommended as preservatives, a hydrotropic substance being defined as one containing both a hydrophilic group and a hydrophobic group having an affinity for organic solvents.

According to a recent statement by Twiss (155), the Dunlop Rubber Company makes considerable use of latex concen-

trated after compounding. He states that "concentrated compounded" latex has a uniform composition, is free from undesirable tendencies to gravitational separation, and is capable of producing goods of considerable thickness by a dipping or spreading process with a small number of coats. In the preparation of this material, Twiss states that the initially fluid compounded latex is maintained throughout the evaporation process in swirling movement to keep the compounding ingredients in uniform dispersion. According to Warren (163), the Twiss concentrator, which has been called "the latex prototype of the ordinary mixing mill" (155), consists of a jacketed stainless-steel bowl with water circulating in the jacket. Hot air is blown into a hollow lid from which it is distributed through perforations to the surface of the latex. Concentrated compounded latex, having a total solid content of 70 to 80 per cent, can be made by this process (156).

Worthy of mention also is the recent proposal of Twiss and Murphy (157) for concentrating latex to a water content of 3 per cent or less. In this process the water is largely replaced, during evaporation, by polyhydroxy compounds such as glycerol or diethylene glycol. These liquids serve as media in which the added protective colloid (e. g., soap) continues to function after the water content has become quite low. The reversible concentrate so produced may be rendered irreversible by molding or kneading.

The possibility of making, by a spraying process, the ideal concentrated latex—a dry powder which can be dispersed in water—has not been overlooked. Carrington (34) discusses the spray-drying of Revertex, whereby there is produced a reversible powder which can be peptized by dilute ammonia. Nyrop (115) has protected a process for obtaining a reversible concentrate by spraying latex simultaneously with a suspension of protective agents and fillers. A latex-hemoglobin mixture may also be spray-dried to give a reversible powder according to Wescott (167). The unfortunate disadvantage of spray-dried powders of this nature is their pronounced instability towards pressure.

CENTRIFUGING. Among centrifuging processes, that of Utermark (159) seems to have been given the greatest commercial exploitation, the product obtained by this method having been on the market for some time. In discussing the process used, Carrington (34) states that latex treated with about 0.3 per cent ammonia is centrifuged at about 8000 to 9000 r. p. m. The product, which has a total solid content of about 60 per cent, has been freed of much of its protective matter, and must therefore be handled with care.

Wescott (164) has proposed the addition of such a material as hemoglobin or Irish moss to protect the latex and at the same time to aid separation in the centrifuge. Another patent by this investigator combines centrifuging and spray-drying. In this process the latex, treated with hemoglobin, is

concentrated and then sprayed into an atmosphere of low humidity. The resulting product may have a cheeselike appearance or be in the form of a dry noncoherent powder which may be redispersed, preferably by dilute ammonia.

De Vries and co-workers (160) report that rubber made from centrifuged latex has a slow rate of drying, is generally light in color, has low tensile strength and slow rate of cure, ages rather poorly, and (contrary to previous claims) is not especially uniform. Of practical interest is the fact that this rubber is decidedly plastic. In this connection, de Vries and Beumée-Nieuwland (160) state that centrifuging is the only method to date for producing a plastic rubber that has no tendency to deteriorate on storage.

CREAMING. The creaming of latex is analogous to the creaming of cow's milk, although separation takes place more readily in the latter case. Although latex, preserved with ammonia, creams only on long standing, that preserved with sodium hydroxide does so very readily. Since most of the protective serum constituents remain in the lower layer, the cream is quite unstable. Carrington (34) states that rubber from creamed latex has chemical properties resembling those of smoked sheets or pale crepe, whereas its physical properties in the vulcanized state approach those of sprayed latex both before and after aging.

Although evaporation and centrifuging processes have so far been given greater commercial development, the number of recent patents on creaming processes indicate an increasing interest in this latter method of concentrating latex. The usual procedure is to add a creaming agent to hasten the separation. According to the patent literature (159, 174), substances which facilitate separation of the rubber globules in latex include glue, gelatin, carrageen moss, Iceland moss, Irish moss, pectin, gum arabic, Karaya gum, alginic acid, various alginates, and buffer solutions, such as a mixture of primary and secondary sodium phosphates. McGavack (108) has recently protected by patent the idea of repeatedly using the serums from creaming operations in new creamings, thus reducing the requirement of creaming agent. It is claimed by Hauser that separation is more satisfactory when the creaming is carried out above 90° C. Hill and co-workers (60) report that, although vulcanized latex creams unsatisfactorily, the addition of creaming agents with the vulcanizing agents will effect good creaming during vulcanization and subsequent standing. The addition of about 25 per cent of natural latex is also said to facilitate the creaming of vulcanized latex. A somewhat radical proposal—that of the I. G. Farbenindustrie Akt.-Ges. (88)—is to cream by rapidly adding acids until a pH value less than 2 is attained. The viscous paste, which can be separated from the serum by filtration after standing 24 hours, is said to be redispersible in dilute ammonia.

FILTRATION. Filtration as a method of concentrating latex does not appear to have been used commercially. A

recent patent to Pestalozza (121) covers a process in which latex is passed back and forth between two containers and is exposed to ceramic filters during passage. Loss of serum through the filters results in a gradual increase in the rubber content of the material remaining.

INCORPORATION OF COMPOUNDING INGREDIENTS INTO LATEX

Since nearly all of the rubber put to practical use is compounded rubber, the methods of incorporating compounding ingredients into latex are of prime importance. The introduction of these ingredients or pigments (to use the rubber compounders' term) is, in the case of latex, a fundamentally different process from that with crude rubber. A pigment which can be milled into crude rubber with comparative ease may be difficult to distribute uniformly in an aqueous dispersion such as latex. The principal difficulties with compounding ingredients for latex have been attributed by various investigators to electrical charge (e. g., magnesium oxide will discharge and coagulate the negative latex particles); dehydrating power (e. g., carbon black); tendency to settle out; and failure to be wetted by latex. A procedure which lessens one of these difficulties may often aggravate another. In this connection, the writers have observed that passage of the pigment suspension or of the compounded latex through a colloid mill or through a paint mill, will usually improve dispersion and retard settling, but may greatly increase the tendency toward coagulation.

INCORPORATION OF FINE POWDERS. Stevens (143) states that most fine powders, when stirred into latex, coagulate it, the coagulation manifesting itself either as a sudden or a gradual stiffening of the paste. The presence of anticoagulants, such as caustic soda, sodium carbonate, or ammonia, retard this coagulation. According to Stevens, the best method of introducing pigments is to put them into the form of a paste with water or an alkaline solution, before stirring into the latex. Even then the incorporation of certain pigments, such as carbon black and zinc oxide, is very difficult, and resort to the use of protective colloids is necessary. Stevens mentions soap, glue, hemoglobin, and gelatin solutions in this connection. Casein, fatty oils, fatty acids, glue, gelatin, and resinic acids are included in the list of protective colloids given by Wiegand (169). Among the agents which the writers have used successfully may be mentioned gum tragacanth, gum ghatti, potassium soap, and saponin. A certain specificity has been observed in the protective influence which the various colloids exert on the different pigments, an effective agent for one pigment not necessarily being of much service for another.

Several suggestions have been made in connection with carbon black, which is probably the fine powder most difficult to incorporate. According to Wiegand (169), the use of saponin in a carbon black-water paste facilitates wetting and

aids in the subsequent mixing of the paste with latex. A neutral or slightly alkaline solution of cellulose xanthate is also said (47) to be a good medium for dispersing carbon black prior to introducing it into latex. Park's recent suggestion (117) for increasing the dispersibility of carbon black in latex is to treat the black with the vapors of a material such as pine oil or petroleum distillate.

SPECIFIC METHODS FOR INCORPORATING VULCANIZING INGREDIENTS, SOFTENERS, AND OTHER MATERIALS. To facilitate the introduction of sulfur, the large particle size of which is ordinarily objectionable, it has been proposed (49) either to retard settling by introducing bentonite clay into the latex system, to fuse the pigment first with kieselguhr and introduce the ground product thereafter, or to add the sulfur to a vulcanizable oil and then introduce the mixture. The use



Courtesy of Revertex Corp. of America

FIGURE 4. EMPTYING A CHARGE OF FINISHED REVERTEX

of sulfur of particle size much smaller than normal has also been suggested (30). For certain purposes, sulfur may be advantageously introduced into latex in the form of the hydride (28) or of a polysulfide, such as ammonium or calcium polysulfide (143).

The same general considerations apply in the case of accelerators as with inorganic compounding ingredients. Since water-soluble accelerators can be mixed with latex very readily (provided they are not of such a nature as to coagulate the latter), it is often desirable to use this type. In the case of latex articles which are formed to shape and which therefore do not require any further processing, such as milling or calendering, the field of applicability of ultra-accelerators is much greater than with articles made from crude rubber. The specific suggestions of Murphy and Twiss, of Grove-Palmer, and of others (172) for accelerators suitable for latex

include the diethyl-ammonium salt of diethyldithiocarbamic acid, dithiofuroic acid and dithiofurates, mercaptobenzo-thiazole, and certain ultra-accelerators which are zinc salts and which therefore require no zinc oxide for activation. Aumarechal and Robrieux (18) propose forming accelerators in preserved latex by causing carbon disulfide or certain aldehydes to react with the ammonia or aromatic amine preservative present.

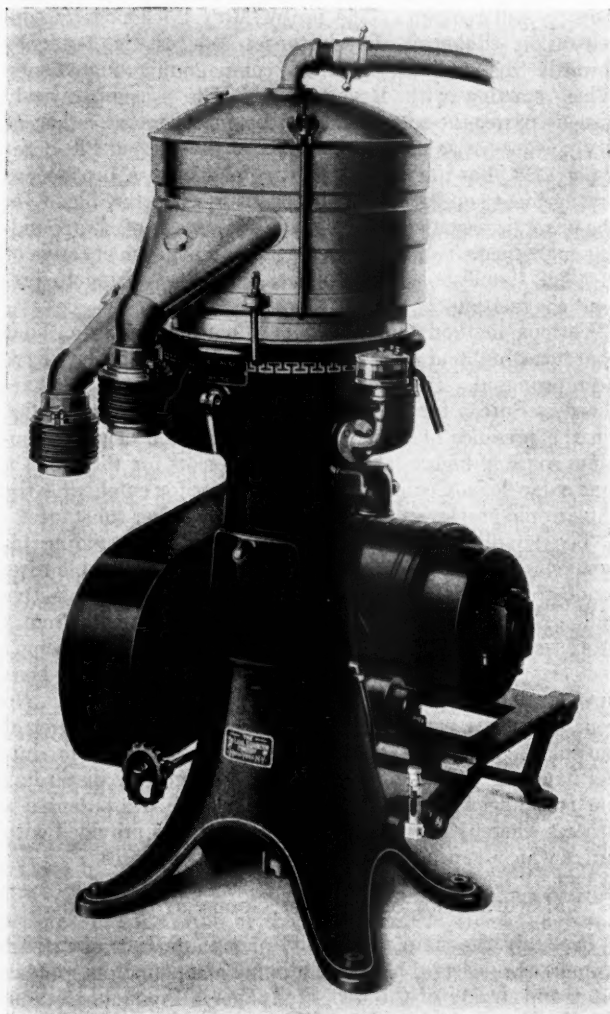
For the coloring of articles made from latex, it is said (173) that almost any dyestuff carrying a negative charge may be used, provided the latex is vulcanized at or near ordinary temperature by use of super-accelerators. Insoluble dyes may first be run through a colloid mill with a protective colloid, or dissolved in a suitable organic solvent and the solution then emulsified. Lakes may be used if in a fine state of subdivision. To employ vat dyes, it is necessary to agitate the mixture of latex and the leuco compound while exposed to the air.

Although the patent literature covers references to the incorporation of various other ingredients, such as selenium, oils, factice, reclaims, wood tars, resins, antioxidants, and stearic acid (19), many of these are not of sufficient interest to warrant discussion in this paper. In general, the waxes, oils, resins, and bituminous materials are neither soluble in water nor can they be introduced in the form of a suspension of fine powders. Emulsification is the usual expedient employed, the nonrubber constituents of the latex sometimes serving as the emulsifying agent. Karaya gum and saponin are additional emulsifying agents which have been used by a number of investigators. Worthy of mention is Gibbon's suggestion for adding stearic acid to latex by first forming ammonium stearate and stirring in the latter. Szegvari's method for introducing resinous antioxidants, such as that formed by condensing aldol with a naphthylamine, is to dissolve them in "rubber oil" (an oily product obtained by the dry distillation of rubber), and emulsify the solution before mixing into latex.

SPECIAL METHODS OF INTRODUCING PIGMENTS. Although the normal procedure in compounding latex is to mix the ingredients into the latex directly with a stirrer of some type, other methods for compounding have been investigated. Chapman and Patterson (39) have made a novel suggestion for the introduction of pigments usually difficult to incorporate. The pigments are first milled into reclaimed rubber or other plastic material, a water dispersion of the compounded stock is formed, and the latter is mixed with latex. Another proposal is to add the pigments on a mill having a fluted roller, which manipulates the latex and continuously exposes new surfaces (91).

One method of introducing compounding ingredients, which is feasible for latex but not for crude-rubber compounding, is to form the ingredient in the latex (or in water im-

mediately before addition to latex) by a double decomposition or similar reaction between two soluble substances. Especially attractive in this connection are reactions, such as that between barium sulfide and zinc sulfate, in which both products formed are insoluble and of interest as rubber pig-



Courtesy of DeLaval Separator Co.

FIGURE 5. CENTRIFUGAL SEPARATOR OF TYPE USED FOR CONCENTRATING LATEX

ments. Patents issued to English and American interests (90) cover the production of such ingredients as barium sulfate, cadmium and other sulfides, lithopone, silicic acid, various silicates, calcium oxalate, and calcium and other

carbonates by this method. It is claimed that white or colored stocks with mechanical properties equal to those of stocks containing carbon black may be thus produced.

METHODS FOR PREVENTING SETTLING OF PIGMENTS. After the compounding ingredients have been dispersed satisfactorily in latex, the problem of keeping them in suspension still remains. The use of latex thickened by concentration (Revertex, for instance) reduces the tendency towards the sedimentation of compounding ingredients. When starting with Revertex, which is a comparatively viscous paste, the pigments may be incorporated either as dry powders or as pastes in a mixer of the Werner-Pfleiderer type (72). For introducing the dry pigments, a brush-sieve arrangement, operating simultaneously with the blades of the mixer, is recommended. If the percentage of compounding ingredients is high, extra water or a solution of casein or of alkali should be added continually during mixing to prevent coagulation.

Various methods for thickening normal latex (without concentrating) and thus retarding the settling of fillers have been proposed. Included among these suggestions (183) are those of Sutton for thickening with finely divided zinc oxide (in the presence of ammonia), of Teague for using ammonium soaps of higher fatty acids, of Wescott for the use of a zinc oxide-hemoglobin gel, and of Hauser for employing the thixotropic properties of bentonite clay or other substances.

The handling of ordinary latex, after compounding ingredients have been incorporated, requires considerable care. Aside from their previously mentioned function, protective colloids may help to retard the settling of pigments from a latex suspension. Methods for pumping and thus keeping the suspension in circulation to avoid settling have been developed by the Dunlop Company and others (53). No general remedy can be given for the ever-present danger of partial coagulation of the sensitive pigment-latex system during handling. To avoid the necessity of entirely discarding partially agglomerated latex, Szegvari (147) has patented a process whereby it is circulated through tanks provided with filters which continuously remove the agglomerates.

MANUFACTURE OF RUBBER GOODS BY DIPPING

Probably the simplest method of manufacture of articles from latex consists of alternate dipping of a nonporous mold in latex and drying of the deposited layer. Products made in this manner have found increasing use and are, at present, competing quite successfully with goods made by dipping in rubber cements. Among the articles made by this method may be mentioned surgeons gloves, electricians gloves, finger cots, coated screens, and balloons. As is the case when dipping in rubber cements, the chief disadvantages are that the latex flows after the mold is removed from the bath, causing unevenness in thickness, and that the thickness of the layer ob-

tained by a single dip is very slight. Robertson (125) has succeeded in avoiding the former disadvantage by regulating the speed of withdrawal of the mold from the bath so that the latex film sets by the time the mold is completely withdrawn. Increasing the thickness of the film obtained by a single dip or decreasing the time necessary between the dips have been the subject of much investigation during the past few years. The methods discussed below have been suggested for these purposes.

CONCENTRATION AND THICKENING OF LATEX FOR DIPPING. Hadfield (68) has increased the efficiency of the dipping process by using a heated mold in a concentrated vulcanizing latex with alternate dipping and drying of the surface of the deposit. Twiss (154) also used concentrated latex but, instead of alternate dipping in latex and drying, used alternate dipping in latex and in a coagulant. As previously discussed, he is of the opinion that concentration after compounding gives a better product for the purpose than compounding after concentration.

Use of thickening agents, such as polysaccharides, albuminoids, or plant extracts, to facilitate dipping has been made (4). Hauser has used bentonite for this purpose (77).

DIPPING WITH ACCOMPANYING OR SUBSEQUENT COAGULATION. Mention has already been made of the method of alternate dipping in concentrated latex and in coagulant used by Twiss (154). The same worker has used molds covered with either a coagulant-containing jelly (154) or a solution of a coagulant, and, in conjunction with Murphy and Thorpe (158) has advanced the idea of an alternate dipping and coagulating with a volatile coagulant. Methods similar to the latter have been advocated by MacKay and Thorpe (103) and by Teague (149).

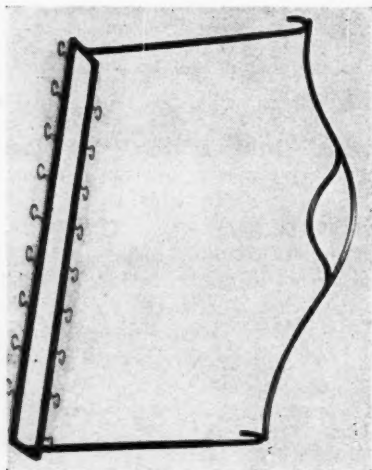
In all the above methods, care must be taken in washing in order to assure complete removal of the coagulant prior to cure, as otherwise the rate of cure and aging of the resulting product are adversely affected.

DIPPING IN CONJUNCTION WITH HEAT. One of the most interesting methods of facilitating the production of rubber articles by dipping has been proposed by Pestalozza (119). Heat-sensitive latex is prepared by adding solutions or suspensions of salts of bi- or trivalent metals. Upon the introduction of a heated form, the adjacent latex is heated and coagulated. The thickness of the coagulated layer may be controlled by varying the time of dipping or the temperature of the former. A similar method has also been suggested by Chapman, Murphy, Pounder, and Parkes (38) who propose the use of ammonium persulfate, with or without trioxymethylene or sodium silicofluoride as sensitizing agents. Trowbridge (153) has found that the use of a heated form in untreated latex is advantageous. Campbell (33) has been able to obtain deposits of appreciable thickness by applying heat and pressure to latex in a mold. Specific mention is

made of the applicability of this process to the manufacture of tubes.

MANUFACTURE OF RUBBER GOODS BY DEPOSITION FROM AGGREGATED LATEX

A very interesting modification of the dipping process has recently been developed in this country. Usually the deposition of latex on porous molds is an exceedingly slow process, since the latex particles are of such size that ultra-filters must be used. Even with ultra-filters the process is difficult, as the resistance to flow of serum through the deposited layers becomes very high as the layer increases, and the deposition becomes progressively slower. Owing to the deformability of the latex particle, the deposit becomes compact if high pressure is used.



Courtesy of Miller Rubber Co.

FIGURE 6. ELECTROPLATING RACK COVERED WITH RUBBER BY ANODE PROCESS

These difficulties are avoided, and deposition is made comparatively simple by increasing the effective size of the particles. This is accomplished by aggregation of the latex particles into relatively large groups (55). A number of means have been described for obtaining aggregation; probably the first of these is the one described by Hopkinson and Gibbons (33). Organic colloids, such as Irish moss, were found to promote aggregation, especially if considerable quantities of pigments, such as whiting, were present. The same workers (34) have also found that by freeing latex of ammonia and adding small amounts of phenol and trisodium phosphate, aggregation and increased filterability are obtained after one month.

Smith (139) found that buffer solutions of primary and secondary sodium phosphates were effective when a sufficient quantity was added to decrease the pH of the latex to approximately 6. Further decrease in pH resulted in increased filterability and decreased stability down to the point where coagulation occurred. Cadwell and Hazell (32) have used aldehydes, such as cinnamic, butyr- and furfuraldehydes to obtain aggregation. Greenup (67) has mentioned the use of boric acid for the same purpose. According to Hazell (78), greatly increased filterability is obtained by treating latex with zinc oxide or zinc salts, and alkali sulfides or polysulfides followed by stirring and heating. The manufacture of inner tubes by a process similar to the above has been described by Hopkinson and Gibbons (84).

ELECTRODEPOSITION

PROCESS IMPROVEMENTS. The electrolytic deposition of rubber upon the anode is well known and is the subject of numerous patents. Many of these are concerned with overcoming difficulties encountered in the practical application of the process. Gas formation is one of these, as it causes porosity in the final product. It is also necessary, according to Klein (95), to obtain constant conductivity, alkalinity, and rubber content, for the best results.

One of the first remedies (2) used to prevent gas formation and porosity was to deposit the rubber on a hollow porous mold around the electrode, gas being formed at the electrode but not on the mold. A second method, which consists in using current potentials below the decomposition potential of water, has been suggested by the Anode Rubber Company (3) and by Williams (171), but this means increased time for deposition. Beal and Sheppard (20) have protected the use of artificial cooling to permit the use of higher potentials. Klein and Szegevari (97) add materials, such as sodium thiosulfate, which react with the oxygen liberated. Cowper-Coles (44, 45) has used intermittent deposition with removal of the anodes between successive depositions to permit the removal of gases. This yields a compact layer. According to the same worker, the conductivity of the deposition bath is improved, and a softer deposit is obtained when ammonium acetate is added. Softer and less compact deposits are also obtained by the addition of soft soap, according to Klein and Healy (96). Shellac is said by Jenny (87) to increase the adhesion of the deposit to metals, while, according to Davies (46), co-deposition of synthetic resins and rubber yields products of characteristics quite different from those of the usual deposits. The thickness of deposited layer in a given time is increased by the addition of starches, glue, and dextrin according to the Toto Company (150).

MODIFICATIONS OF ELECTRODEPOSITION PROCESS. Several modifications of the electrodeposition process have recently

been suggested. These consist of cathodic deposition, alternating current deposition, and internal current deposition.

Cathodic deposition is, as its name implies, deposition of the rubber particles upon the cathode. This is accomplished by deposition from latex in which the electrical charge on the particles has been reversed (54). James and Twiss (86) have used such materials as acetic acid and formaldehyde in conjunction with protective colloids for this purpose, while the Siemens-Elektro-Osmose Gesellschaft (137) has used thorium nitrate.

The use of alternating current for deposition is made possible by using two different materials, such as aluminum and carbon, for electrodes. According to Madge, Round, and Twiss (104), a partial rectification of the current takes place. Deposition with alternating current has also been proposed by the Siemens-Elektro-Osmose Gesellschaft (137).

Still another modification of the anode process is that of Williams (170) in which the deposition bath is itself the source of current. Ammonium chloride is added to the latex in such quantity that coagulation does not occur. Carbon and zinc are used as the electrodes. When the circuit is completed, a current flows through the cell, and rubber is deposited.

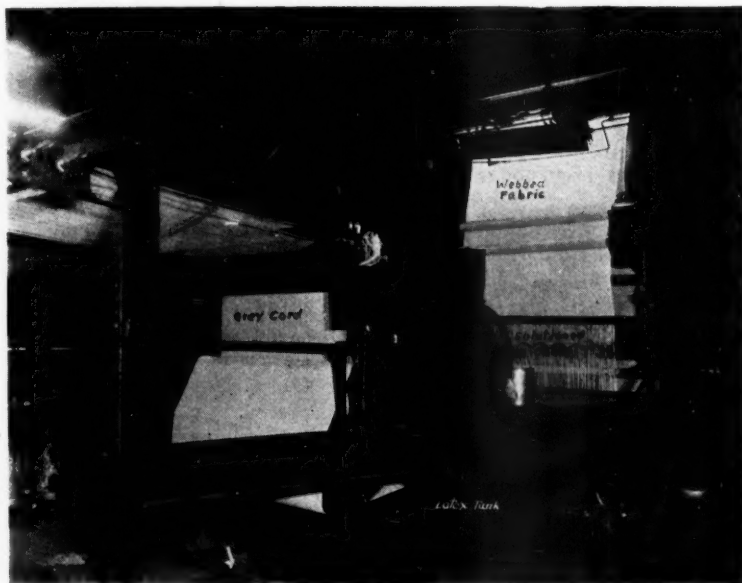
OTHER METHODS OF MANUFACTURE

GELLING. Although the gelling of latex or compounded latex cannot alone be classed as a method of manufacture, it has been investigated as a preliminary step in the production of porous and other types of articles by molding, spreading, dipping, spraying, etc. By the gelling process, the consistency of the latex is so changed that manufacture of the final article is often facilitated. A sharp distinction cannot always be drawn between a gelling process and the thickening processes discussed in the section on Incorporation of Compounding Ingredients in Latex, although the function of the thickening is primarily to retard the settling of pigments, rather than to facilitate any specific manufacturing operation. According to patents granted to Davies; Teague; Wescott; Gabor; Beckmann; McGavack; Hayes, Madge, and Jennings; and others (47, 177, 183), there are quite a number of substances which have a gelling effect on latex. Among these may be mentioned formaldehyde (alone or mixed with such substances as phenol and tannic acid), silicic acid, sodium silicofluoride, alum, calcium chloride, magnesium sulfate, saponin, gelatin, agar-agar, carrageen moss, hemoglobin-zinc oxide mixture, hemoglobin alone, other proteins and albumens, and cellulose xanthate. The time required for the gelling to take place varies with the agent used. Some of the materials, such as hemoglobin, also require a moderate heating.

In fact, the addition of agents having little or no effect at room temperature, but a gelling or coagulating action at a somewhat higher temperature, has been the subject of a number of patents granted to Pestalozza (119) and to certain

English investigators (56). Although a considerable quantity of a salt of a bi- or trivalent metal will coagulate latex in the cold, a smaller portion will merely have a slight thickening effect. Further thickening and, finally, coagulation are said to take place as the temperature is raised toward the boiling point. The nature of the agents used for this purpose has been discussed under the subheading, Dipping in Conjunction with Heat. It is claimed that latex so treated can be used satisfactorily in the direct production of rubber goods not only by dipping but also by extrusion and by introduction into heated molds.

MOLDING. The manufacture of molded articles from compounded latex is often difficult, since the consistency of



Courtesy of United States Rubber Co.

FIGURE 7. LATEX-DIPPING OF CORD FABRIC TO BE USED IN MANUFACTURE OF TIRES

the mixture is frequently too thin. The water content, moreover, is usually too high, unless a porous product is desired. It is necessary, therefore, either to gel the mixture to obtain the proper consistency or to coagulate it partially and remove the excess water. Patents, respectively illustrative of these two methods of surmounting the difficulties mentioned, have been issued to McGavack (107) and to Loomis and Stump (101). According to a process protected by the Dominion Rubber Company (51), molded articles may be made by coagulating the latex in molds and drying at a moderate temperature. By using concentrated compounded latex, Carrington (34) states that mats, sheets, etc., can be

molded by direct drying, an empirical allowance for shrinkage being made. Careful control of the water content of the mixture is, of course, necessary.

EXTRUDING. The manufacture of articles such as threads and tubes by extruding the properly compounded latex into a coagulating or dehydrating bath offers possibilities which appear to have received no great amount of attention in recent years. Patents issued to Murphy and Twiss (112) cover a process which consists in allowing concentrated compounded latex to flow by gravity through an orifice under the surface of a setting or dehydrating bath. The specific gravity of the bath, which in a typical case may contain sodium chloride and ammonium acetate, is so adjusted that the coagulated rubber rises to the surface. By using a die with an annular orifice, it is said to be possible to extrude a tube.

SPRAYING. Rubber manufacturers have become more or less familiar with crude rubber prepared by spray-drying, the process for which has recently been described in some detail by de Leeuw (98). Of more interest in connection with the present discussion is the suggestion of Stevens (144) that the rubber "snow" (the initial fluffy product settling to the bottom of the spray chambers) may serve as a molding powder from which certain rubber articles may be manufactured by a direct process. When it is considered that compounded latex can also be sprayed, the possibilities of a spray process for the manufacture of articles from latex become broader. Theoretically, the number of articles which might be manufactured by spraying compounded latex into molds or upon formers of suitable shape is very large. The possibility of using a spray process in the manufacture of inner tubes, solid tires, hose, and rubber-coated articles has been discussed by Hauser (71). The spray process appears to be particularly adaptable for the production of rubber coatings on objects which are of such intricate shapes or are in such inaccessible positions that other methods of coating cannot be used.

The difficulties attending the spray method are sufficient, however, to have limited its use thus far to a relatively narrow field. Notable among these difficulties are clogging of the spraying devices, lack of smoothness in the dried film, and a tendency toward a lack of uniformity in the product. It is the writers' experience that sheets formed by the spray-drying of latex containing compounding ingredients are often striated. Stocks containing a high proportion of pigments often exhibit a low tensile strength after being spray-dried and vulcanized. A brief period of milling of the dried stock before vulcanization has been observed to increase the tensile strength considerably. Rupture of the individual rubber globules and the consequent improvement in the dispersion of the solid ingredients probably account for the increase.

Means of overcoming at least a part of these difficulties have been worked out. Carrington (34) states that the tendency

toward premature coagulation in the spraying jets may sometimes be avoided by simultaneously spraying two different suspensions, each of which contains only a part of the final composition. One of the recent patents issued to Maynard (106) describes a spraying device so constructed that a continuous stream of latex is blown off the bottom of a rounded tip. Clogging is claimed to be avoided by this device. The production of inner tubes by a spraying process is covered by another patent granted to this same investigator.

MILLING AFTER COMPOUNDING AND COAGULATING. Despite the fact that one of the main objects of investigations involving latex has been to obviate the use of mixing mills in



Courtesy of Dewey and Almy Chemical Co.

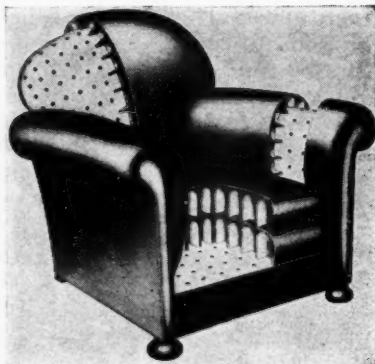
FIGURE 8. LATEX-BONDED BRAKE AND CLUTCH LININGS

the rubber industry, the possible combination of latex compounding and subsequent milling of the dried latex stocks has not been overlooked. As pointed out by Twiss (155), the latex particles retain enough of their individuality after drying the compounded latex so that the foreign particles tend to remain outside the globules rather than to penetrate them uniformly. By using suitably protected latex, it is possible, according to Twiss, to introduce very large quantities of carbon black (100 per cent or more on the basis of the rubber present). The crumblike coagulum (118), which forms, resembles the spray-dried stocks discussed above in that it does not exhibit the properties of reinforced rubber upon being dried and vulcanized. According to Twiss, milling of such a

stock for 2 or 3 minutes suffices to distribute the carbon black within the rubber globules so that reinforcement is at once manifest. Hauser (72, 74), who has also proposed a brief period of milling for stocks made from compounded concentrated latex, has pointed out that good tear resistance is not to be expected from a dried latex stock which is so heavily compounded that the latex particles are entirely covered by pigments.

IMPREGNATION OF FABRIC

The impregnation of fabric with rubber by means of latex dipping was naturally one of the first uses suggested for latex. After a few trials it became evident that, instead of true impregnation of the individual fibers, only a superficial coating was obtained. Dieterich (50) was able to show by



Courtesy of Dunlop Rubber Co., Ltd.

FIGURE 9. CHAIR UPHOLSTERED WITH CELLULAR AIR CUSHIONS MADE FROM LATEX

(Partly in section to show construction.)

means of photomicrographs that this was the case, while Hauser and Hünemörder (75) came to the conclusion, after studying microscopically the rubber left upon removal of the cotton with sulfuric acid, that even less impregnation was obtained with latex dipping than with frictioning. The poor impregnation has been attributed to the different electrical charges on the fabric and latex particles, and consequent coagulation on the surface of the fabric.

Although true impregnation is not obtained in this manner, Schidrowitz (129) is convinced that certain advantages are offered in the treatment of cords or fabrics with latex. Gibbons (64), using the United States Rubber Company's flexing machine, has shown that from the standpoint of flexing life, latex-treated web fabric is far superior to cord fabric of the same construction.

Numerous means have been tried for obtaining true impregnation. Biddle (26) has found that the use of pressure is advantageous, while Trowbridge (152) has passed dipped fabric over a porous plate with simultaneous application of vacuum to force the latex into the cords. An attractive method of obtaining a coating of the individual fibers is that of Bongrand and Lejeune (27) which consists of applying the latex on the spinning frame while the fibers are in the roving stage. The twist for converting the rovings into thread is given after the impregnation. Although the process appears very promising from the theoretical standpoint, a considerable number of mechanical difficulties would have to be overcome before its practical application could be assured.

Another method of obtaining impregnation, which has received considerable attention during the past three years, is that of impregnating with latex to which a wetting agent has been added. These wetting agents, which are polar compounds, are adsorbed on the latex particles and prevent the latter from being adsorbed on the surface of the fabric. It is evident that they influence markedly the interfacial tension between fabric and latex. Among those materials which have been used are sulfonated oils, sodium sulfanilate, thiourea, orthotoluidine, ammonium linolenate, saponin, and soluble salts of sulfonic acids, such as sodium isopropyl naphthalene-sulfonate, and sodium butyl naphthalenesulfonate with liquid alcohols (148). Some of those suggested, although strong protectives against coagulation with pigments or dilute electrolytes, are valueless for obtaining true impregnation.

USES FOR AND PRODUCTS FROM LATEX

The actual and potential uses for and the products from latex, which have been described in the literature of the past five years, are so numerous that many of them can receive no mention whatever in this article. Such uses as have been previously discussed are given little, if any, further attention in this section. The attempt has been made to confine the discussion largely to those uses which have either received extensive development, offer the greatest promise, or possess novelty.

LATEX IN TIRE AND TUBE MANUFACTURE. The latex used in impregnating cord fabric (Figure 7) constitutes a considerable proportion of the total amount of latex imported into America (13). The possibility of manufacturing other parts of a tire (such as the tread) from latex seems to have received more discussion than actual development (34, 112, 118).

The manufacture of inner tubes appears to be a more feasible proposition. The fact that latex inner tubes were marketed in small quantities by one of the large American rubber companies as early as 1928 gives indication of the commercial possibilities of such a process. The possible manufacture of tubes by electrodeposition has been extensively investigated by another company. The literature

indicates, furthermore, that two of the other large rubber companies in this country have been interested in the possibilities inherent in latex inner tubes (67, 127). It seems, therefore, that the use of latex in the manufacture of inner tubes might be considerable, were it not for the fact that latex (with its high cost of transportation) is placed at a decided disadvantage by the low cost of rubber.

OTHER LATEX PRODUCTS FOR AUTOMOBILE INDUSTRY. Other latex products which are of particular interest to the automobile industry, and which have been developed beyond the experimental stage, include latex-bonded brake and clutch linings (14). According to Wescott's patent (166), they are manufactured from latex and asbestos fiber. (See Figure 8.)

Recent reports indicate that latex has invaded the field of automobile manufacture even further. It is now being utilized in the production of the sponge-rubber seats used in certain English cars (8). The rubber base for the mohair upholstery used in some automobiles is now also made from latex.

CEMENTS, ADHESIVES, AND SEALING COMPOUNDS. One of the largest uses for latex at the present time is in the manufacture of adhesives and sealing compounds. Practically all the sealing compounds are used in the sealing of cans. The merits of such compounds have been fully discussed by Hauser (71). According to Cord (42), sealing compounds may be made by adding fillers such as kaolin, talc, asbestos, or barium sulfate to the latex. The American Can Company (1) has used a thickener such as sodium alginate in conjunction with fillers such as aluminum oxide. Dewey (48) has vulcanized latex, added bentonite clay, and used the products as a sealing compound. Egan and McGowan (59) have found that mixtures of latex and solid peptized fillers are satisfactory. Aluminum oxide, when mixed with sodium silicate, is said by them to be a suitable filler.

The use of latex in the shoe industry has grown so rapidly in the past five years that at the present time latex cements are available for every cementing operation. It is said (10) that over twenty different types of cements are used for such operations as fitting and stitching, lasting, making, packing, wood-heel building, welting, heel building, and applying sole leather. Sutton (145) has stated that the best method of attaching shoe soles is by using latex in conjunction with a self-vulcanizing rubber cement. The leather is given a coat of latex and, when dry, a coat of rubber cement. After the joint has been made, the vulcanizing agents migrate from the cement and vulcanize the latex. It is claimed that a permanent joint, unaffected by the weather, is obtained. Still another method is advocated by Cavanaugh (37) who applies latex to the surfaces and unites them with pressure after drying. This method is said to be especially applicable for attaching shoe heels. Many of the shoe cements in use today

contain thickeners, such as bentonite clay, and tack producers such as resins and pitches.

One of the processes, recently developed for attaching rubber to metal, calls for the use of a latex-protein cement. Wescott (165) found that a mixture containing 50 parts of rubber in the form of latex, 40 parts of hemoglobin or certain other proteins, and 10 parts of vulcanizing agents would cause satisfactory adhesion. Levin (100) used formaldehyde to harden a cement of latex and albumen, and applied heat to effect coagulation of the albumen and make the bond. Carson (36) has also made cements of latex, hemoglobin, tanning material, and vulcanizing agents. The usual procedure for applying is to coat the metal with a layer of cement, dry, bake at a temperature considerably above 100° C., and apply a coat of rubber cement and then the rubber stock. The bond is completed during the cure. Cements of this sort have been used for attaching rubber wringer rolls to the metal shafts and in rubber-metal automotive parts.

Revertex particularly has found considerable use as a waterproofing cement in the textile industry (111). Two layers of cloth are bound and waterproofed by an intervening layer of Revertex applied by spreading. In some cases penetration catalysts such as have been mentioned in the discussion of the impregnation of fabric are used. The rubber layer is cured by passing the plied material through strongly heated calenders. Similar cements are being used in applying a backing to artificial leather or rayon.

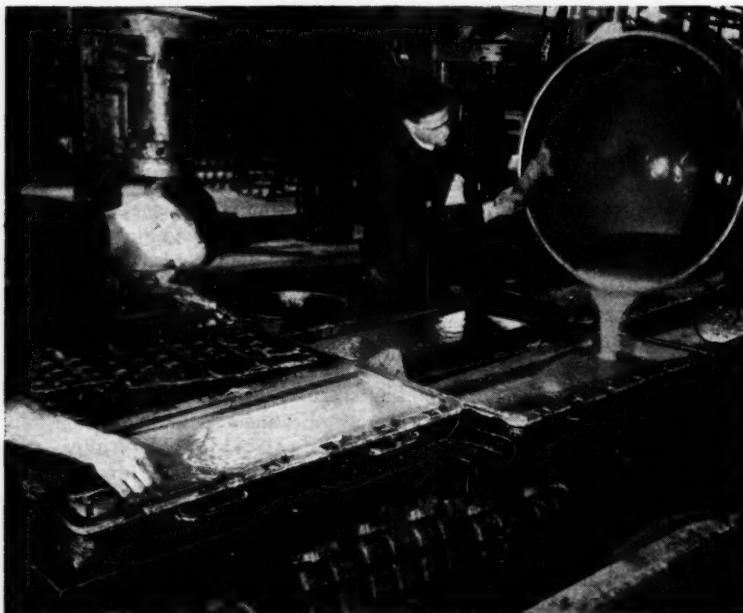
Cements made from latex have found numerous other applications. A mixture of latex and bentonite clay has been on the market for some time as an adhesive for attaching paper labels to tinned containers; while Dry Seal, a latex adhesive for envelopes, is claimed to be economical and to retain its adhesiveness for five years if kept free from dust (6). Mathey and also Johnson and Johnson (89) have proposed to make an adhesive from latex by successive creaming with gum tragacanth and addition of formaldehyde and sodium silicate. Biddle (25) has proposed to make adhesives from latex, casein, and sodium silicate; from latex, tapioca meal, and lime; and from latex, casein or albumen, and an "insolubilizing" agent, such as an alkaline earth hydroxide. Reitz (123) prepared an adhesive from latex by treating it with the vapors of an aldehyde, while Whittelsey (168) has added rubber solvents to latex in the presence of an emulsifying agent. Similarly, Traube (151) used a rubber solvent in the presence of gall or gall-containing materials.

POROUS AND SPONGE-RUBBER PRODUCTS. As early as 1914, Schidrowitz and Goldsbrough (130) found that, by vulcanizing coagulated latex in steam, a porous product was obtained. They also formed a product which contained both macroscopic and microscopic pores, by adding carbonates to the latex prior to coagulating with acetic acid.

A more recent but somewhat similar process is the one

developed by Beckmann. It consists of coagulating or gelling latex and curing in steam or moist vapor so that syneresis does not take place. In this way the network structure of the gel is retained.

Several agents for gelling latex have been found. Among them may be mentioned magnesium sulfate, calcium chloride, zinc sulfate, alum, ferric chloride, manganese salts, sulfur dioxide, and gaseous and liquid acids (21). In order to prevent local coagulation, to delay setting, and to yield a firmer gel, casein, blood albumin, hemoglobin, and other protective colloids are used (23). Materials which are capable of being coagulated to form hydrophilic gels may also be added. For example, silicic acid, tannic acid, aluminum hydroxide,



Courtesy of Dunlop Rubber Co., Ltd.

FIGURE 10. POURING COMPOUNDED LATEX FROTH INTO MOLDS DURING MANUFACTURE OF CELLULAR AIR CUSHIONS

colloidal ferric oxide, and hemoglobin have been mentioned (23). The gels may be toughened by exposure to sulfur dioxide or volatile acids.

The porous material obtained by this process possesses unique properties (24). It has been estimated that, in the case of a porous rubber containing 40 per cent of rubber by volume, some 500,000 pores occur in each square centimeter of surface, and that the average diameter of the pores is 0.0004 mm. The porosity of the cured rubber is controlled by the dilution of the latex. It has been found possible to make products with from 15 to 85 per cent of their volume as voids.

Both soft and hard rubber articles are made. As far as the writers can ascertain, the largest use is for storage battery separators, where the chemical resistance of the hard rubber and the low electrical resistance of the highly porous material are of advantage. Battery separators are now made from latex in Germany and in England. It is understood that they are being experimented with by several of the leading battery manufacturers in this country.

Among the other products made of this material may be mentioned filters, bath mats, and oil-bearing wicks.

A recent development in the field of sponge rubber products made from latex is that of the Dunlop Rubber Company (56a). In this process a frothing agent such as soap and a gelling agent such as sodium silicofluoride are added to concentrated or thickened latex. The mixture is beaten into a froth with a mechanical beater and poured into a mold of the desired shape. It is then allowed to gel at room temperature prior to drying or is simultaneously gelled and dried by heating in the open air at 95° C. If desired the product obtained may be given a further vulcanizing by heating in steam. The material obtained differs from that made by the Beckmann method in having its structure composed of closed cells instead of having a network structure.

Several practical applications have been found for the material made by this process. As illustrated by Figures 9 to 12, it is used for automobile cushions and furniture upholstery.

LATEX IN THE INSULATION INDUSTRY. Although the use of whole latex in the manufacture of electrical insulating material has been patented, the most significant development involves the use of deproteinized latex. Nuttall (114) states that in the case of hard rubber the breakdown voltage can be increased 300 to 400 per cent by an initial treatment of the latex with caustic soda to destroy the proteins present. His assumption is that the proteins, when present, tend to prevent that maximum polymerization during vulcanization which is desirable for a good dielectric material. According to Kemp (94) Paragutta, the remarkable new insulating material for submarine cables, etc., contains a certain portion of deproteinized rubber. The best deproteinized rubber can be made from latex, the nitrogen content of the rubber produced being less than 0.1 per cent. The method of K. D. P., Ltd., (92) for improving the insulating properties is to remove the serum constituents from the latex by dialysis, while that of Sheppard and Beal (136) is to wash thoroughly rubber deposited from latex.

LATEX IN THE SHOE AND LEATHER INDUSTRIES. Although the most thoroughly developed application of latex in the shoe industry is undoubtedly as latex cement, the possibilities of additional uses are numerous. Composition soles may be made (181) by using latex either with felt, with long cotton fiber, with tire scrap, or with silicon carbide or other abrasive

substances. Darex soles, which are made of felt and compounded latex, are said not to mark floor surfaces, to be waterproof, and to be free from a tendency to spread. According to the process described by van der Schuyt (135), sole crepe may be made by spraying latex from a series of small jets upon a conveyor. To the uniform layer obtained, cork, leather, felt, or other nonskid material may be added mechanically. A material which consists of cotton fiber treated with latex is specially prepared for insoles, middle soles, etc. This material, which is marketed under the name of "Laflex," is also manufactured in the form of cutting blocks to replace the wooden cutting blocks of the shoe and other industries.



Courtesy of Dunlop Rubber Co., Ltd.

FIGURE 11. REMOVING CELLULAR SPONGE RUBBER FROM MOLDS AFTER GELATION AND VULCANIZATION OF LATEX COMPOSITION

According to other suggestions having to do with the shoe industry, latex may be used in the manufacture of heels and linings, and even in the production of shoe laces (118, 131, 131).

In connection with the leather industry in general, it has been stated (29) that a two-color effect may be produced on leather by applying compounded latex to the depressions in the leather after embossing. A proposed compound for finishing leather also contains latex (138).

The use of latex in the manufacture of artificial leather or substitutes for leather has been given considerable attention. When Schidrowitz visited this country in 1928, he exhibited many articles made from artificial leather of this type. In

compositions of this kind, the latex is usually either mixed with stiffening agents, such as casein or cellulose xanthate, or used as a binder for such materials as leather scraps or pulped rabbit skins (173). Imitation leather may also be made from cloth or paper and latex.

LATEX IN PAINT MANUFACTURE. A latex-bitumen composition, which can be diluted and used as a paint, was shown at the Public Works Exhibition in London in November, 1931 (151). Furthermore, it is understood that experiments with paint containing latex have been in progress in the Middle East for some time.

Recent patents covering latex as an ingredient of paint have been issued to Ayres (19), Hopkinson and Teague (35), Traube (151), and others. Latex has been suggested as the base for certain paints, whereas with others it is merely one of the ingredients added to some other base material. The paint vehicle of Traube is a gel obtained from latex, a gall solution, and an organic solvent, such as turpentine.

LATEX IN PAPER AND RAYON INDUSTRIES. The paper industry was one of the first to be invaded by latex. The Kaye process for the manufacture of paper was discussed in the literature as early as 1922. In this process the latex used as a binder imparts to the paper exceptional resistance to breaking, tearing, and folding. According to Hauser (71), this process has not fulfilled its early promise, since the product soon loses its superiority on aging. He states that paper made with vulcanized latex should have a greater capacity for withstanding aging. According to recent patents issued to Kaye, Ross-Wright, Ruderman, and others (179), latex is of value not only as an ingredient to be mixed with the paper pulp in manufacture, but also as a constituent of compositions for the sizing, waterproofing, and greaseproofing of the paper sheets. It is understood that considerable latex is being used by one of the largest paper companies in America.

The possibility of incorporating latex with viscose or similar materials in the manufacture of artificial silks has been discussed by Dreaper and by Iwasaki and Masuda (52). Experiments carried out in Japan indicate that a small amount of latex in viscose will increase the strength of the spun thread, whereas a larger quantity will result in decreased strength and a milky-white color.

LATEX IN MANUFACTURE OF CARPETS, RUGS, AND RUBBER FLOORING. Another development of considerable interest involves the use of latex in the manufacture of rugs and carpets. According to a recent discussion of this process (11), the object of the treatment of the back of cut-pile carpeting with latex is to penetrate the structure of the back of the goods and embed the loop of the pile yarn securely in a rubber bond. The latex treatment also coats the back of the carpeting with a layer of rubber which prevents slipping. It is said that this type of carpeting possesses another unusual advantage, in that rugs of any size and shape can be built up from a

dealer's stock of one width, since the cut edge will not ravel. Furthermore, the properties are such that damaged portions of a rug can be cut out and replaced readily without marring the general appearance. In a similar connection, Fisher (61) reports that latex-impregnated animal hair is being used for stair treads. Even in cases where latex has played no role in the original manufacture, compositions containing this material may still be of service in producing a nonslipping rug. Application to the back of the rug may be by brush or spray-gun (141).

The use of latex in the manufacture of rubber flooring has been the object of some investigation. Although the production of latex mixtures which can be applied in a paste form in manufacturing the completed floor has been discussed, the actual developments in the use of latex appear to have been more closely along the lines of the usual rubber flooring. According to the suggestions (180) in the literature, latex may be used either with sand or sawdust to make flooring blocks; with asbestos, clay, or wood in a flooring composition; or as the top layer of a flooring having a fibrous base. It is further reported that a recent development has made possible the manufacture of rubber flooring and mats from Revertex and ground scrap rubber (124).

Latex appears also to have distinct possibilities as a binding material for the more conventional forms of rubber flooring—i. e., those made from compounded crude rubber. According to a recent statement (7), a satisfactory method of attaching rubber flooring to a base, such as wood or concrete, is to coat the base with properly stabilized latex, allow the latter to dry, and then treat with naphtha before applying the flooring. Beckmann (22) has gone one step further by proposing to coat the underside of the rubber flooring first with a layer of sponge rubber (made from latex), the function of the spongy layer being to aid in the attachment of the flooring to the base when using glue or other binding agents.

PRODUCTS OF ELECTRODEPOSITION PROCESS. The number of articles manufactured entirely or in part by the electrodeposition process is rather large (80, 163). Among these may be mentioned various types of tubing; electricians' gloves; surgeons' gloves; gloves for use with corrosive liquids; and many rubber-coated articles such as door handles, telephone receivers, inspection-lamp cases, pliers, filter-press plates, fan blades, conoidal fans for handling corrosive fumes, spinneret tubes for the rayon industry, screens for corrosive liquids, racks for electroplating, dipping baskets, and intricately shaped articles. It will be apparent from the previous discussion of electrodeposition that this process is peculiarly suitable for the manufacture of many of these articles. (See Figure 6.)

VULCANIZED LATEX AND ITS USES. The vulcanization of latex by the so-called Vultex process was developed by Schidrowitz a number of years ago. By this process there is ob-

tained a vulcanization of the dispersed rubber globules of the latex without appreciable alteration in the colloidal condition of the system. The possible methods of application of Vultex are consequently about as extensive as those of ordinary latex. Manufacture is usually simpler when Vultex is used, however, since drying (without vulcanization) suffices to complete an article, once it has been formed to shape. A further advantage in the use of vulcanized latex is that it can be employed with fine fabrics and with many dyes and pigments which would be destroyed by the heat employed during vulcanization.

The more recent developments in connection with the process of vulcanizing latex have had to do largely with modifications in the accelerator and in the form of sulfur used,



Courtesy of Dunlop Rubber Co., Ltd.

FIGURE 12. TRIMMING VULCANIZED AND DRIED CELLULAR CUSHIONS (MADE FROM LATEX)

and with applications of the process to concentrated latex (28, 184). Ultra-accelerators which have been recommended for vulcanizing latex include tetramethylthiuram disulfide, piperidinium pentamethylenedithiocarbamate, and salts of thiol acids. Sulfur may be added not only in the sublimed, precipitated, or colloidal form, but also as polysulfides, or even as the hydride. Twiss (155) states that, despite repeated expressions to the contrary, it is impossible to vulcanize latex by the action of sulfur dioxide and hydrogen sulfide by a method similar to that of the Peachey process. His explanation is that the nascent sulfur is formed in the water phase and leaves the rubber globules unaffected.

According to the recent literature (40, 141, 161), Vultex is of use in the manufacture of nonslipping rugs, hospital sheeting, imitation leather, impregnated fabrics (which are water-proofed, improved in resistance to wear, and prevented from raveling), rubber soles, golf balls, electrical insulation, dental rubber, latex cements, meteorological balloons, and various forms of dipped goods (such as surgeons' gloves, fountain-pen ink sacs, toy balloons, and druggists' sundries). A development still in the experimental stage is that of the manufacture of inner tubes from vulcanized latex.

MISCELLANEOUS PRODUCTS FROM LATEX. In addition to the previously described use of latex in can-sealing, this material may be of service in the manufacture of other products used in sealing containers. Thus latex has been suggested for use in connection with the production of rubber stoppers, milk bottle stoppers, rubber-lined bottle caps, and artificial corks. An even more radical suggestion which has been made is the sealing of tropical fruits in a film of dried latex before transporting them. Spoon (142) states that this process has not proved very successful, the latex coating sometimes having a tendency to affect the flavor adversely and to promote rather than retard the growth of molds.

For use in manufacturing operations in general, there are a number of products in the making of which latex may be used. Abrasive wheels and other abrasive articles, driving belts, packings, gaskets, and rubber-impregnated ropes are examples (79). The use of the serum from latex as a binder for finely divided molding material, such as sand, is said to be advantageous.

Chewing-gum base is a material which is now being made from latex, hydrogenated oils, and certain other ingredients (146). In this process the latex and other ingredients are continuously agitated while being heated to expel the water. This latex base has been found to be of particular value in the production of the so-called bubble gum, which has gained considerable popularity with children.

The prevailing low price of rubber has further stimulated interest in rubber roadways. A paving of rubber which could be applied in the same manner as is asphalt would appear to be a very interesting type. According to the recent literature, such pavings are being investigated in America, and have been tried on an experimental scale in Singapore (15). Somewhat similar to the use of latex in paving is its suggested use in compositions for covering athletic grounds and for filling expansion joints (43).

Patents covering the manufacture of transparent rubber articles indicate that latex constitutes a desirable raw material for the purpose (5). The use of ultra-accelerators permits of vulcanization at a low temperature. Furthermore, ultra-accelerators, which are of the zinc salt type and which therefore obviate the necessity for adding zinc oxide, can be used. (Excess zinc oxide is deleterious to transparency.)

An added advantage of latex is that, if desired, it can be dialyzed before use to remove part of the colored serum substances.

Further indication of the broad possibilities of latex as a raw material is contained in the references to its use or suggested use in diverse fields (175). Thus, Liesegang has employed latex in the production of certain emulsions in the photographic industry. Latex makes its contribution to music in the form of rubber-impregnated wood for violin manufacture, and to medicine as an anatomical injection fluid and as a raw material for the manufacture of radium applicators. Book binding with latex is feasible, according to Grammer. That latex may even be of service as a lubricant, when mixed with petrolatum, is indicated by preliminary experiments conducted by the Rubber Growers' Association.

In conclusion, attention should be called to the manner in which latex has been invading some of the newer industries (175). In connection with the aviation industry, for instance, porous ebonite (made from latex) may be used in the manufacture of light rubber board for airplanes. The Trans-Lux Daylight Picture Screen Corporation has been granted a patent for the production of a projection screen by spraying a latex composition upon a suitable fabric base. The ideal gas mask of the future will, according to Barker, have its rubber parts manufactured from latex. The radio industry also now has an opportunity to take advantage of this useful material, since a process for the manufacture of latex-impregnated diaphragms for loud speakers has been patented by Fagan. Perhaps the most interesting feature of all is the fact that America's newest large-scale industry—the manufacture of dirigibles—has placed reliance on latex (35). The precious helium of the U. S. S. Akron is retained by fabrics of very low permeability, in the preparation of part of which latex was one of the materials used. Although latex was off to a late start industrially, it is certainly now keeping up with the times.

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Variations in Plantation Sheet Rubber

R. O. Bishop and R. G. Fullerton

Examination of Exhibition Samples

An examination of the vulcanization properties of samples of smoked sheet exhibited at the Malayan Agri-Horticultural Exhibition in August, 1931, led to the collection of data summarized in Table I.

Procedure.—Samples of not less than 5 lb. were taken at random from each case of 224 lb. and vulcanized under the standard conditions now adopted by the Institute and described in the appendix. In the table are also included the results of smoked sheet prepared in August and collected from two estates which did not exhibit. Columns 1 and 2 give serial numbers referring to the various estates, and column 3 gives the thickness of the smoked sheet. Column 4(a) states the time of cure in minutes giving the maximum tensile strength at break, while column 4(b) gives the maximum tensile strength at break in kilograms per square millimeter. A true comparison, however, of the tensile properties of the sample is obtained by reference to column 5, which states the tensile strengths obtained at an elongation of 650 per cent when the samples are vulcanized under uniform conditions, *viz.*, at a cure of 80 minutes. This value is termed the "modulus."

Results.—From the analysis of the results we find by comparison of the coefficients of variation (C. of V.) given at the foot of each column:

- (1) The variation in thickness is decidedly high.
- (2) The variation in rate of cure is 14, and the average rate of cure lies between 80 and 90 minutes.
- (3) There is considerable uniformity in the values for the maximum tensile strength at break.
- (4) The variation in modulus is high.

Discussion.—The most illuminating of these results is No. 4, which shows that the samples vary in their response to vulcanization and exhibit a significant lack of uniformity.

Eaton and Bishop¹ made a similar study of samples of smoked sheet collected from the Malayan Agri-Horticultural Exhibition, 1927. Although the technic adopted at that time for mixing and vulcanization differed from our present practice, a comparison of the results on a common basis shows the same order of variation.

As an indication of the degree of variation which may be obtained in uniform rubber due to methods of vulcanization adopted, we quote in Table II the results obtained for different portions of a sheet of sole crepe selected at random from a case of 100 lb., prepared by one estate, whose crepe invariably fetches top market price. In sampling, the sheet of crepe was rolled tightly into a cylinder and eight samples of 200 g. each taken by cutting sections perpendicular to the axis. The end portions were neglected. From each of the eight portions, a mix was prepared and the eight mixes were vulcanized separately at 100 minutes. Each mix gave four portions for vulcanization, from each of which two rings were taken for testing. The table quotes the loads, in kilograms per square millimeter, obtained at an elongation of 650 per cent. The analysis of the figures given at

TABLE I
SMOKED SHEET
Samples Exhibited at M. A. H. A. Exhibition 1931

1	2	3	4(a)	4(b)	5
R. R. I. Ref. No. H.	Estate No.	Thickness of Smoked Sheet, Mm.	Cure Giving Maximum Tensile Strength at Break, Min.	Maximum Tensile Strength at Break, Kg./Mm. ²	Tensile Strength at 650% Elong- ation at 80 Minutes, Cure, Kg./Mm. ²
848	1	1.89	120	1.55	..
849	2	2.34	90	1.46	0.62
850	3	2.81	80	1.49	1.29
851	4	3.84	80	1.51	0.88
852	5	3.23	80	1.56	1.08
853	6	3.96	80	1.36	1.04
854	7	3.56	90	1.66	0.69
855	8	3.38	90	1.51	0.52
856	10	2.64	90	1.49	0.77
857	12	3.44	90	1.58	0.60
858	13	4.25	80	1.47	0.99
859	14	4.33	70	1.52	0.94
860	15	3.93	90	1.32	0.62
861	16	3.56	80	1.49	0.99
862	17	2.36	80	1.50	1.00
863	18	3.88	120	1.39	0.48
864	19	3.18	90	1.47	0.77
865	20	2.44	80	1.45	0.64
866	21	4.60	70	1.40	0.76
867	23	3.22	90	1.50	0.77
868	24	2.82	90	1.34	0.55
869	25	3.96	80	1.44	1.10
870	26	3.35	70	1.42	0.69
871	27	3.79	70	1.21	0.79
872	29	4.12	80	1.46	0.88
873	30	2.69	90	1.41	0.72
874	31	3.99	90	1.46	0.62
875	32	3.00	60	1.37	..
876	33	2.38	80	1.53	0.91
877	35	2.42	80	1.12	0.56
878	36	3.20	80	1.45	0.71
879	38	3.71	80	1.53	0.87
880	39	2.82	80	1.50	0.84
881	41	3.79	80	1.45	0.67
882	42	3.73	80	1.47	0.82
883	43	2.86	90	1.31	0.58
884	44	2.93	80	1.28	0.59
885	45	3.41	80	1.22	0.43
886	46	2.95	80	1.44	0.75
887	47	3.19	70	1.30	0.65
888	48	3.51	70	1.37	0.83
889	49	2.62	80	1.34	0.62
890	50	3.50	80	1.46	0.79
891	65	3.06	80	1.36	0.74
892	66	3.43	105	1.27	0.46
1031	67	..	90	1.32	0.82
..	68	2.81	90	1.48	0.78

Mean = 3.28 Mean = 83 Mean = 1.43 Mean = 0.76
 S. D. = 0.604 S. D. = 11.14 S. D. = 0.104 S. D. = 0.185
 C. of V. = 18 C. of V. = 14 C. of V. = 7 C. of V. = 24

$$\text{S. D.} = \sqrt{\frac{\sum d^2}{n}}$$

$$\text{C. of V.} = \frac{100 \times \text{S. D.}}{\text{Mean}}$$

TABLE II
SOLE CREPE

Loads in Kg./Mm. ² at 650 Per Cent Elongation at 100 Minutes' Cure					
Mix No.	Loads				Mean
1	0.96	0.99	0.97	0.96	0.97
	0.96	0.99	0.97	0.99	
2	0.92	0.92	1.01	0.91	0.93
	0.92	0.91	0.95	0.94	
3	0.98	0.95	1.01	0.97	0.98
	0.94	0.93	1.05	1.01	
4	0.86	0.84	0.90	0.88	0.85
	0.87	0.84	0.87	0.85	
5	0.94	0.93	0.97	0.96	0.94
	0.93	0.92	0.90	0.95	
6	1.02	0.98	1.02	1.04	0.97
	0.99	0.95	0.97	0.96	
Mean = 0.95					
S. D. = 0.05					
C. of V. = 5					

the foot of the table shows that the variation in the values obtained is very low, the coefficient (C. of V.) being 5, compared with a coefficient of 24 for the M. A. H. A. Exhibition samples.

Examination of Rubber from Selected Estates

The nature of the results recorded above led us to investigate the variation in rubber prepared on the same estate at different times. From eight of the estates on the M. A. H. A. Exhibition list further cases of smoked sheet of 224 lb. each were collected from crop manufactured early in November. The methods of sampling the cases were similar to those adopted in August, and the two sets of results are presented for comparison in Table III. It will be seen that only in one instance—that of estate No. 4—has the rate of cure remained unaltered, while for estates Nos. 26 and 27, rubber which had in August a rate of cure higher than the average is now in November lower than the average, the difference being 20 minutes. In this connection it should be noted that in August the sheets were very much thicker and less uniform in thickness than those prepared in November. In the other samples examined, the rate of cure has altered to the extent of 10 minutes. The values for maximum tensile strength at break have not substantially altered. The extent of the changes may be appreciated by reference to the modulus figures in column No. 4.

TABLE III
COMPARISON OF AUGUST AND NOVEMBER SHEET

1 Estate No.	2 Thickness of Smoked Sheet, Mm.		3(a) Cure Giving Maximum Tensile Strength at Break, Min.		3(b) Maximum Tensile Strength at Break, Kg./Mm. ²		4 Tensile Strength at 650% Elongation at 80 Minutes' Cure, Kg./Mm. ²	
	Aug.	Nov.	Aug.	Nov.	Aug.	Nov.	Aug.	Nov.
8	3.38	3.03	90	80	1.51	1.37	0.52	0.61
4	3.84	3.59	80	80	1.51	1.25	0.88	0.72
67	90	100	1.32	1.32	0.82	0.49
26	3.35	3.03	70	90	1.42	1.28	0.69	0.58
27	3.79	3.05	70	90	1.21	1.43	0.79	0.42
68	2.81	2.81	90	80	1.48	1.33	0.78	0.83
14	4.33	3.25	70	80	1.52	1.38	0.94	0.87
12	3.44	2.98	90	80	1.58	1.45	0.60	0.67

To ascertain to what extent the changes observed might be due to methods of sampling, cases were collected at random from estate No. 68, and an examination made of portions drawn from different parts of each case. Three cases of 224 lb. each were taken corresponding to different crop dates. The results, summarized in Table IV, indicate that there is a very great lack of uniformity in the rubber in cases Nos. 1 and 2 collected in August, while that in case No. 3 collected in November may be said to be almost uniform in quality, since the variation in load is within the limits of experimental error (*vide* appendix).

TABLE IV
VARIATION IN A CASE OF 224 LB.

Sheet Vulcanized under Standard Conditions at 90 Minutes.
Load per Sq. Mm., Determined at 650 Per Cent Elongation.
Case No. 1 from Sheet Prepared during 1st Week in August.
Case No. 2 from Sheet Prepared during 4th Week in August.
Case No. 3 from Sheet Prepared during 1st Week in November.

Case 1 Load, Kg./Mm. ²	Case 2 Load, Kg./Mm. ²	Case 3 Load, Kg./Mm. ²
1.48	1.31	1.09
1.53	1.21	1.07
1.44	1.16	1.09
0.71	0.96	1.03
0.70	1.07	1.07
		1.09
Mean = 1.17	Mean = 1.14	Mean = 1.07
S. D. = 0.40	S. D. = 0.12	S. D. = 0.02
C. of V. = 34	C. of V. = 11	C. of V. = 2

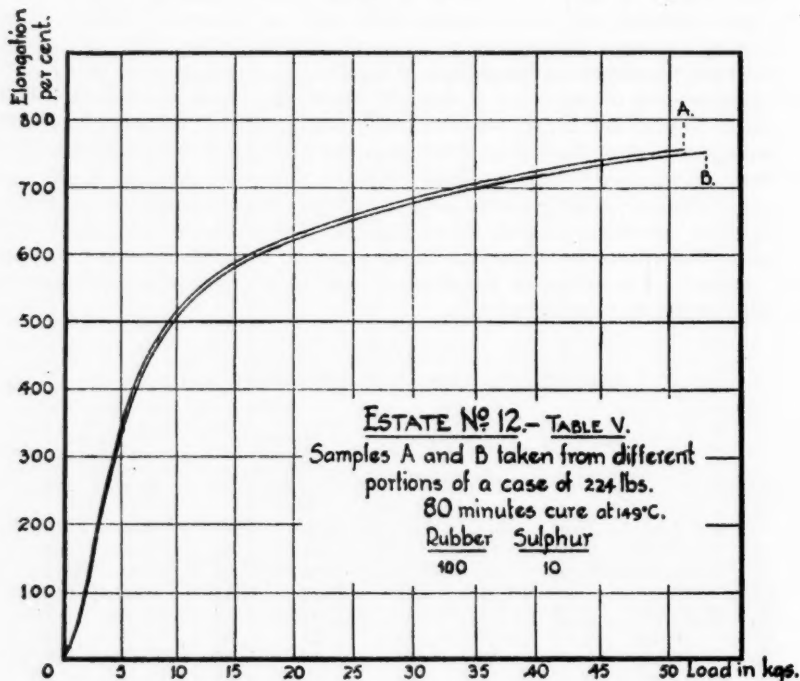
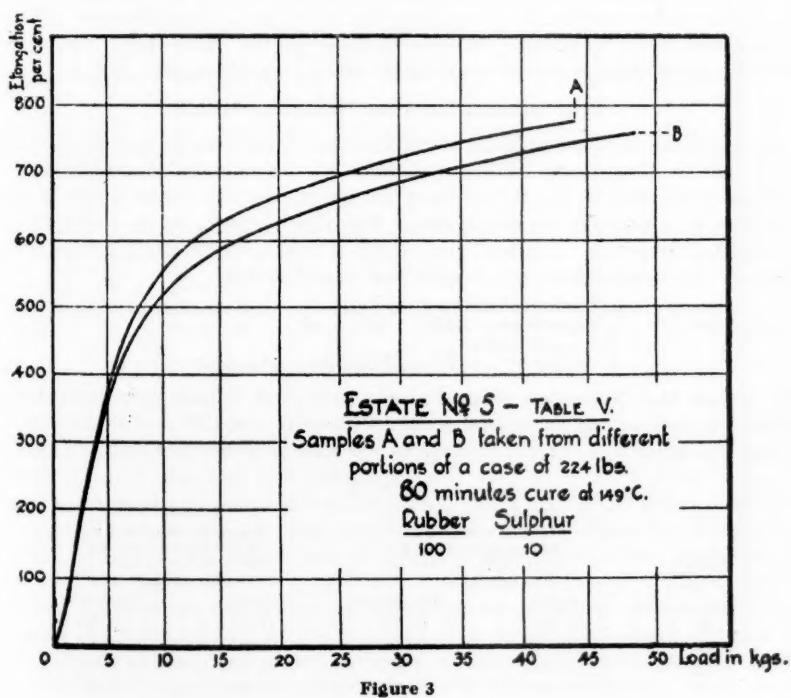
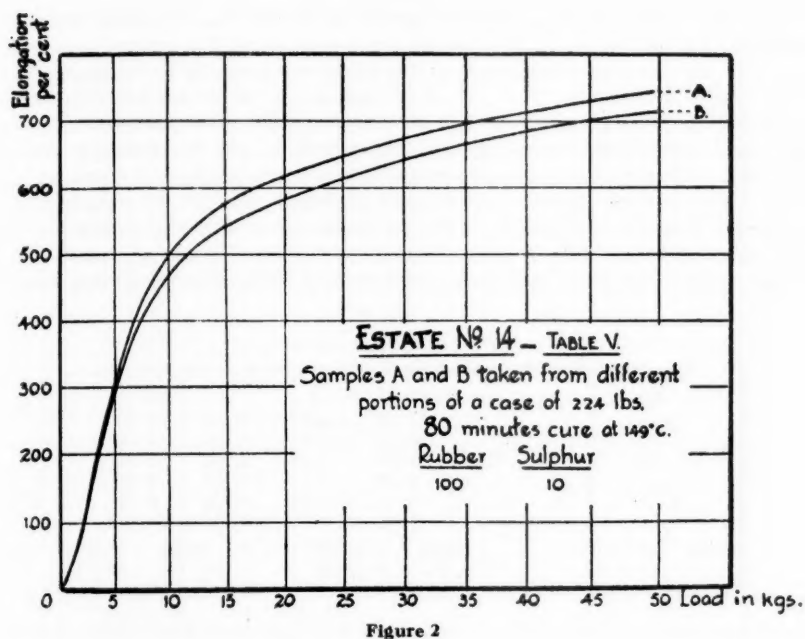


Figure 1



Since we were aware that factory practice on estate No. 68 was in process of alteration during the period, August–November, we decided to extend our investigation to the examination of cases of smoked sheet prepared in November from three estates among the M. A. H. A. exhibitors on which we know that good supervision governs manufacture and attention is paid to the processes of bulking the latex, coagulation, machining, and drying with a view to securing a uniform product. As before, samples were drawn from different portions of a case and the loads determined at 650 per cent elongation when cured for 80 minutes. The results are presented in Table V. The coefficients show that the variation in the case collected from estate No. 12 is almost of the same order as that obtained for the uniform sample of sole crepe referred to in Table II. On estates Nos. 14

TABLE V
VARIATION IN A CASE OF 224 LB.

Loads at 650% Elongation at 80 Minutes' Cure—Kg./Mm. ²								
Estate No. 12			Estate No. 14			Estate No. 5		
0.66	0.78	0.64	0.72	0.66	0.82	0.52	0.54	0.61
0.65	0.70	0.71	0.71	0.71	0.91	0.52	0.59	0.68
0.70	0.70	0.67	0.71	0.70	0.88	0.53	0.50	0.66
0.63	0.72	0.75	0.71	0.69	0.77	0.53	0.56	0.73
0.63	0.68	0.76	0.70	0.66	0.85	0.59	0.58	0.74
0.72	0.66	0.80	0.65	0.69	0.89	0.59	0.58	0.71
Mean = 0.70			Mean = 0.75			Mean = 0.60		
S. D. = 0.05			S. D. = 0.08			S. D. = 0.08		
C. of V. = 7			C. of V. = 11			C. of V. = 13		

and 5, however, even when allowance is made for experimental error, the variation is much higher, and in the case of estate No. 5 is almost double that of estate No. 12. Results have been selected to illustrate in Figs. 1, 2, and 3 the differences obtained for samples drawn from two different portions of the same case. The curves show the representative stress/strain relationship for each sample.

Comparisons Based on Technical Mixes

In accordance with the practice of most modern investigators, and as advocated by Martin in his remarks on the evaluation of raw rubber,⁷ it was decided to ascertain the extent of the variations when the rubber was vulcanized in a technical mixing containing an accelerator. For this purpose, as an initial step it was decided to use the "Captax" mix, which is typical of American compounding practice. Its composition on a weight basis is as follows:

100 parts rubber
6 parts zinc oxide
3.5 parts sulfur
0.5 part "Captax" (mercaptobenzothiazole)

The August and November smoked sheets from four estates were compared in this mix, by vulcanizing for 40 minutes at a temperature of 126° C. and determining the load in kilograms per sq. mm. at an elongation of 650 per cent. Table VI

Estate No.	Rubber : Sulfur Mix Load at 650 Per Cent Elongation Cured for 80 Minutes at 149° C., Kg./Mm. ¹		"Captax" Mix Loads at 650 Per Cent Elongation Cured for 40 Minutes at 126° C., Kg./Mm. ¹	
	August	November	August	November
26	0.69	0.58	0.61	0.83
27	0.79	0.42	0.95	0.87
12	0.60	0.67	0.43	1.00
14	0.94	0.87	0.88	1.33

gives the results obtained for the same samples of sheet according to our standard procedure, using a rubber and sulfur mix, while for comparison are given the results obtained with the corresponding "Captax" mixes.

The differences obtained under the two methods of procedure are more readily appreciated by reference to Figs. 4 to 7 (a) and (b) showing the stress/strain relationship for each vulcanized sample. Confirming the results of discussions which we have had with representatives of various large manufacturing concerns, it is evident that it is a difficult matter to correlate the results obtained with a simple rubber-sulfur mix with those obtained with a technical mix containing "Captax." In the case of estate No. 26—*vide* Figs. 4(a) and (b)—the relationship between August and November rubber as shown in a rubber-sulfur mix is completely re-

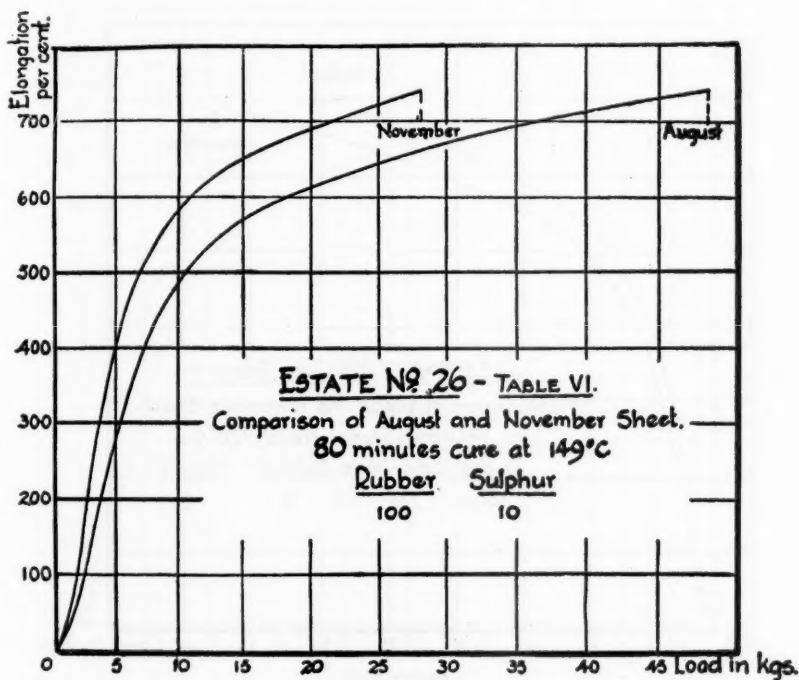


Figure 4 (a)

versed in a "Captax" mix. The difference in moduli of rubber from No. 27 for a rubber-sulfur mix is greater than is the case with No. 26—*viz.*, 0.37, compared with 0.11—and, although the position is not reversed in a "Captax" mix, the curves for August and November rubber are brought very much closer together—*vide* Figs. 5 (a) and (b). In the remaining two estate samples the difference in modulus with a rubber-sulfur mix is much smaller than in the preceding two cases, but the curves for a "Captax" mix are much wider apart. The variations obtained indicate the desirability of expressing the results of vulcanization tests in terms of a standard technical mix as well as in terms of the usual rubber-sulfur mix. The results are reminiscent of those obtained in the vulcanizations carried out on rubber containing variable proportions of different sugars.²

As will be seen, the foregoing results are similar to those obtained by Dinsmore,³ an extract from whose article is given below:

"With the object of providing data on variability, rate of cure was adopted as a criterion, and it was demonstrated that the variation between bales of the same lot of rubber was as great as the variation between different lots. It was shown that there was also considerable variation throughout the rubber in a single bale.

"In further tests carried out to determine the efficacy of blending, tests were made from each of a number of batches of rubber taken from the breakdown mills. In all, 48 samples representing 48 batches were taken over a 7-day period, and were studied in a pure gum "Captax" friction, activated with zinc oxide, with results as follow:

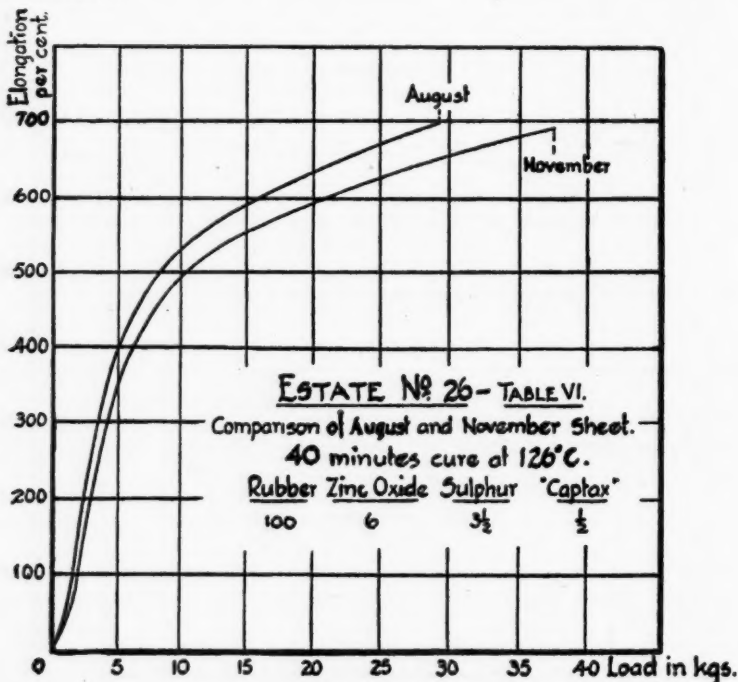


Figure 4 (b)

Tensile,
Kg./Cm.²
 "24 tests between 160-180
 15 tests between 140-160
 9 tests between 120-140

700% Modulus,
Kg./Cm.²
 6 tests between 140-160
 7 tests between 120-140
 18 tests between 100-120

"This shows a rather wide variation even after blending.

"Another check made to see the effect of using a high grade tread rubber which had been tested in the friction formula above, showed these results on 20 samples.

FRICTION TEST—20 SAMPLES

Tests
 "2, between
 1, between
 10, between
 7, between

700% Modulus,
Kg./Cm.²
 160-180
 140-160
 120-140
 100-120

TREAD TEST—20 SAMPLES

Tests	500% Modulus, Kg./Cm. ²
"3, between	170-190
9, between	150-170
8, between	130-150

"Point for point there was a general correspondence between the high and low tests for the two stocks although there were some reversals. Here again the fluctuation is considerable. The above data are typical of a large mass which, unfortunately, time did not permit of condensing to suitable form for this hastily prepared review.

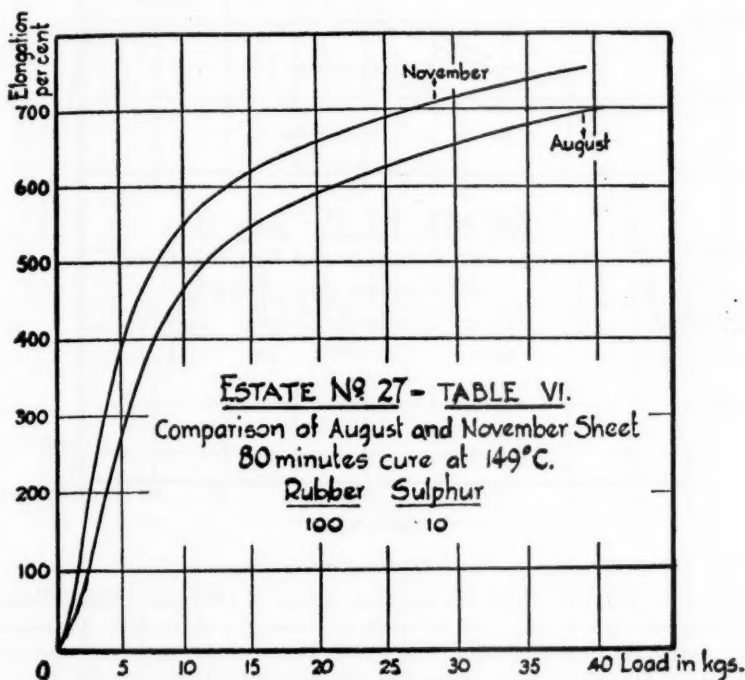


Figure 5 (a)

"It is now pertinent to ask whether these results are reflected in any practical performance tests. Two rubbers were selected by the friction formula, giving moduli of 120 and 57, respectively. These were compounded in a solid tire stock where the differences were apparently entirely eliminated. However, on a blow-out test, the *high* grade rubber gave about 45 per cent more mileage than the *low* grade. Two other rubbers were selected having modulus figures in the friction stock of 147 and 37. Here the solid tire stock showed about 8 per cent difference in modulus, but there was 50 per cent difference in the mileage to blow out.

"In a high-grade balloon tread stock, rubbers which were selected because they gave moduli of 104 and 53 in the friction test, gave 88 and 84 in the tread stock with abrasion loss figures of 10.9 and 11.5, respectively. The road-wear resistance was in the ratio of 112 to 100.

"Another test was made on a pneumatic truck tire carcass for blowout. The rubbers tested 105 and 70 modulus. On a slow speed there was no difference beyond the experimental error. The high-speed test showed a difference of 60 per cent in favor of the high-test rubber."

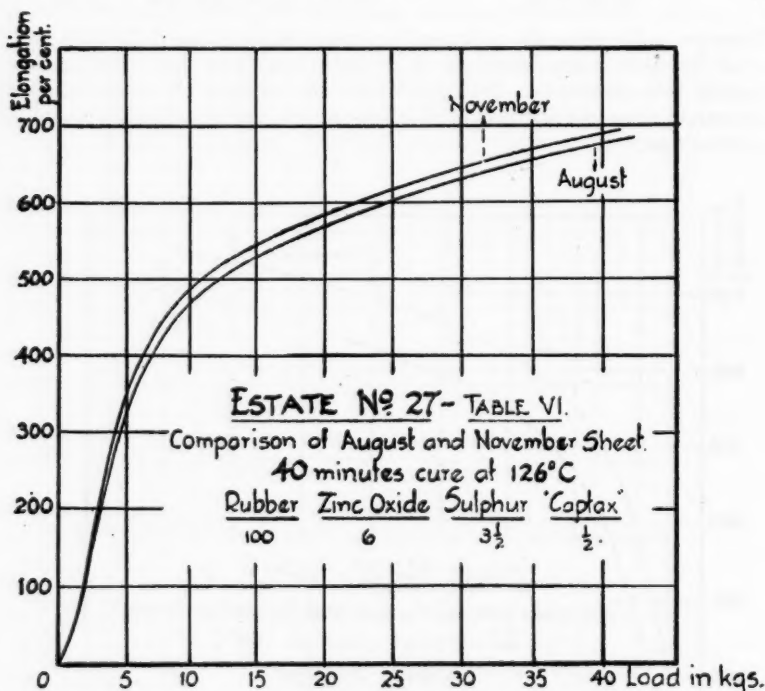


Figure 5 (b)

Discussion

While it is recognized that the adoption of rate of cure and tensile strength of the vulcanized rubber may not be entirely indicative of the true characteristics of any particular type of rubber, it is felt that rate of cure and tensile strength of the product provide a very reasonable criterion for determining the uniformity of any particular product, and there has been sufficient work done to show that the other characteristics of rubber, such as those associated with aging and plasticity, are subject to the same degree of variability. Investigations on plasticity have been carried out in the Dutch East Indies and by the Rubber Research Scheme, Ceylon.^{5,6}

From these results, it is obvious that, in spite of the knowledge we possess and the work which has been done on the preparation of rubber of uniform quality, there is still a very marked variability in the product of even first-class European estates. The divergence of the results recorded for plasticity may possibly be accounted for by the difference in age of the samples tested by the two investigators, but it is also open to assumption that the variations originated in the preparation of the samples.

It is thus evident that one must eliminate variables due to methods of preparation before attempting to compare any two kinds of rubber. The extent of the

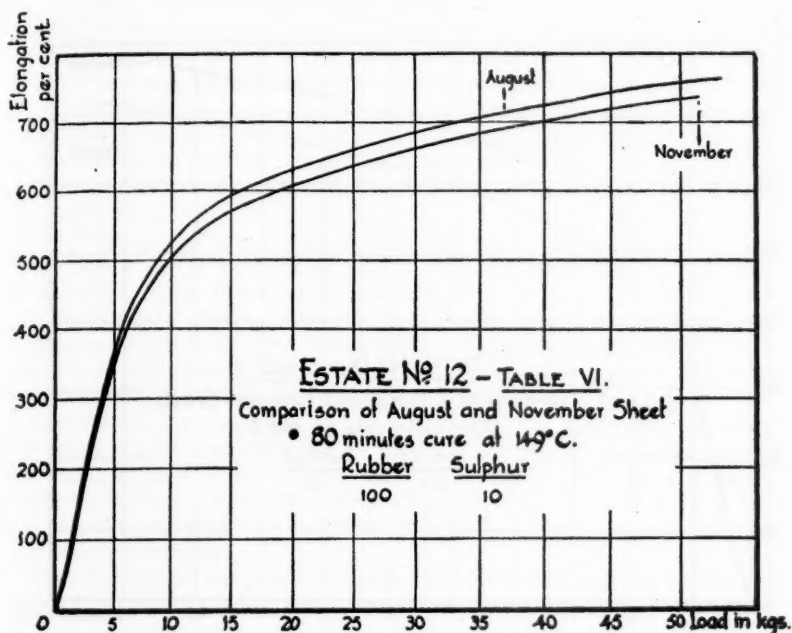


Figure 6 (a)

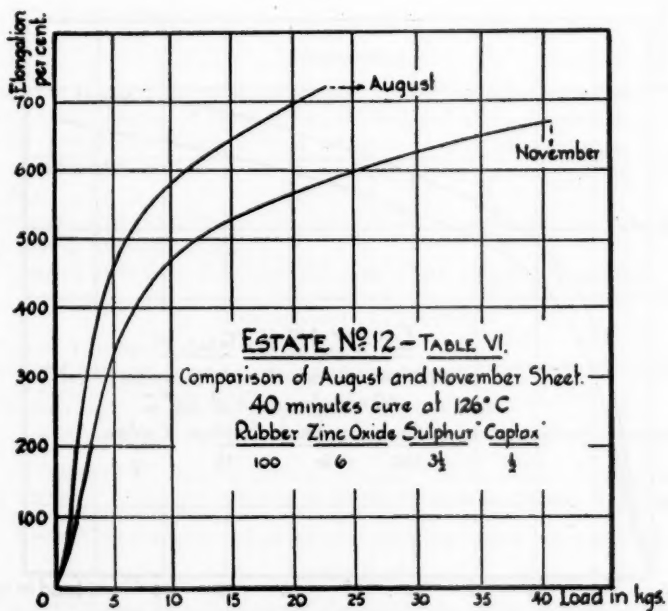


Figure 6 (b)

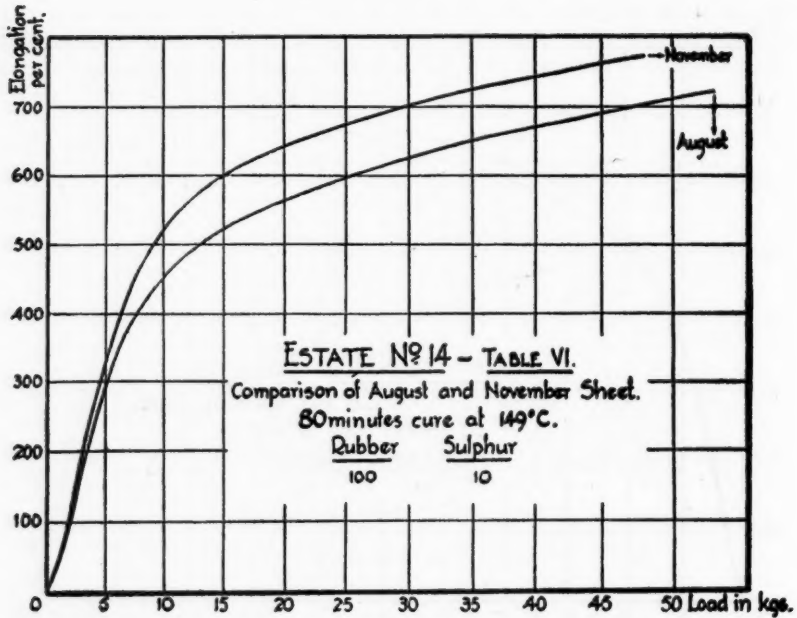


Figure 7 (a)

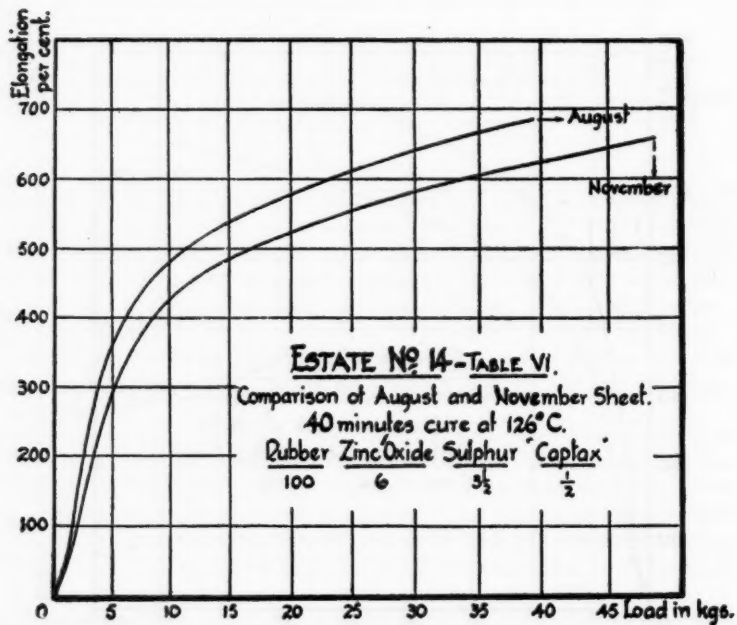


Figure 7 (b)

influence exerted by variations in estate factory practice on the rate of cure and tensile strength of the raw product were sufficiently demonstrated as early as 1914 by Eaton, Grantham, and Day.⁴ Further investigations carried out along these lines show conclusively that it is possible only by precise control of all the operations involved to produce a raw rubber possessing uniform characteristics. The calibration of variability is a first essential in the examination of rubber from different clones of bud-grafted stock and in the comparison of smoked sheet with air-dried sheet.

It is of great significance that, at the present time, when the price of plantation raw rubber is at the lowest level reached since the beginning of the industry, the world consumption of reclaim is yet as high as 36 per cent of the total.

In other words, although the raw product can compete in price with reclaimed rubber, the latter is still very widely used, and there are good grounds for stating that the explanation of this striking fact is that manufacturers find in reclaim desirable properties which are not possessed by plantation raw rubber.

It is outside the scope of this paper to discuss the possibilities of preparing a plantation rubber possessing all the desirable characteristics of reclaim, but it is justifiable, in view of the marked variation in first grade sheet disclosed by the above results, to emphasize the need for standardizing our methods of preparation, whereby the uniformity of our product may be more closely related to manufacturing requirements.

From the results published by previous investigators and the results recorded elsewhere in this Journal,² it has been shown that variability in rubber is caused by the presence of serum substances derived from the parent latex. Therefore, if the product of plantation factories is to be uniform in quality, the proportion of serum components present in the rubber must be reduced to a minimum or to a constant proportion. Modern methods of estate factory practice provide means for accomplishing this.

Summary

An examination of the samples of sheet rubber collected at a recent Exhibition discloses a high degree of variation in the vulcanization properties of the rubber.

Similar variations in the normal produce of first class estates are recorded. Other properties of rubber, such as plasticity, may be expected to show similar variability.

Figures are given to indicate the extent of the irregularities and how they would be reflected in technical mixes.

The bearing of this on the industrial uses of raw rubber is discussed.

References to Literature

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- ³ *India Rubber World*, 79, 77 (March, 1929).
- ⁴ S. S. and F. M. S., Department of Agriculture, *Bulletin*, No. 27.
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- ⁶ O. de Vries and N. Beumée-Nieuwland, "Plasticity Determinations in Crude Rubber. VII. Relation between Structure and Plasticity of Rubber Prepared in Different Ways," *Arch. voor de Rubber Cultuur*, 13, 283-353 (1929).
- ⁷ G. Martin, "The Evaluation of Raw Rubber," *Trans. Inst. Rubber Ind.*, 6, 299-316 (1930).

APPENDIX

The following sample of the form of the certificate which is issued by the Institute on samples sent for vulcanization tests gives a summary of the standards and

technic which have been adopted and which apply to the results quoted in the present article.

Certificate of Quality of Rubber

This certificate is based on the results obtained by the following technic adopted in vulcanization and testing in the Experimental Vulcanizing Laboratory of the Institute.

Mixing.—The standard mixing consists of 20 grams of sulfur and 200 grams of rubber. Three such mixings are made from the sample, and from each mixing 4 equal portions of 40 grams each are obtained for vulcanization.

Curing.—The mixings are kept for a period of 24 hours, after which they are cured in molds in a steam autoclave at 149° C., using a standard N. P. L. thermometer to control the temperature.

Method of Testing.—Twenty-four hours after vulcanization, two rings are cut from each portion of 40 grams by means of a Schopper ring-cutting machine (rotating knives) giving a ring of 3.80 millimeters width. The average thickness of the ring is obtained by a micrometer screw gage applied to the uncut test-piece.

The rings are stretched to the breaking point on a Scott Rubber Testing Machine, which records automatically on a chart the stress/strain relationship for the sample.

Corresponding to each period of cure, 6 rings are tested, and the average of the six results recorded.

Modulus.—This is the load in kilograms per square millimeter obtained at an elongation of 650 per cent at a cure of 80 minutes. This gives a figure which is used to compare different samples. It is more accurate than the figure for tensile strength at break, which is subject to a large experimental error.

Maximum Tensile Strength at Break.—The load at break is expressed in kilograms per square millimeter. (Kg./mm.²)

Rate of Cure.—This is the period of cure which gives the maximum tensile strength at break.

Experimental Error.—The results recorded for modulus are used as criteria for classifying the rubber tested. The actual figures are subject to an experimental error not greater than $\pm 4\%$.

The figures for "maximum tensile strength" are subject to a greater experimental error, and should only be regarded as an indication of the normality of the sample.

The results obtained for the samples in this report may be compared with the following figures, which are the average values for standard types of rubber examined and recorded in the Institute's laboratory.

Type	Modulus or Load at 650 Per Cent Elongation at 80 Minutes, Cure, Kg./Mm. ²	Cure Giving Maximum Tensile Strength at Break, Min.	Maximum Tensile Strength at Break, Kg./Mm. ²
Smoked sheet	0.76	80 to 90	1.43
Unsmoked sheet	0.61	90	1.38
No. 1 crepe	0.60	100	1.37
Fine hard para	0.83	90	1.48

A Method for the Purification of Rubber and Properties of the Purified Rubber

A. T. McPherson

Abstract

Purified rubber was prepared by the digestion of crude rubber or latex with water at about 190° C., followed by extraction with water and with alcohol, and drying in an atmosphere of inert gas. The digestion hydrolyzed the proteins, and the extraction removed the hydrolysis products, resins, and other impurities. The purified rubber contained about 99.5 per cent of rubber hydrocarbon. Properties of the rubber hydrocarbon at 25° C. were: density, 0.9060; refractive index, 1.5184; dielectric constant at 1000 cycles per second, 2.37; power factor at 1000 cycles per second, 0.0015; conductivity at the end of 1 minute, 2.2×10^{-7} mho. The electrical properties measured on 14 samples were apparently independent of the botanical source or the kind of crude rubber.

I. Introduction

This paper describes a simple procedure which was used to purify rubber¹ for a study of the electrical properties of the system rubber-sulfur. The method of purification was one in which the non-hydrocarbon components of the raw rubber were removed by extraction, the proteins being first hydrolyzed by digestion with water at an elevated temperature. The solvents with which the rubber was extracted were water and alcohol. These removed the protein disintegration products, sugars, fatty acids, and other resinous and minor components, and yielded a product which was about 99.5 per cent rubber hydrocarbon. While this method of purification involves no distinctly original features, it is here given in some detail, since it may be of interest to other investigators who may wish to prepare for experimental purposes large quantities of rubber hydrocarbon of reasonable purity without an excessive expenditure of time.²

The dielectric constant, power factor, and conductivity of purified rubber prepared from different kinds of crude rubber were relatively consistent, and showed no variations which might be attributed to the botanical source or kind of rubber.

II. Description of the Purification Process

Various procedures were tried for the purification of rubber from latex or crude rubber. The procedure which proved the simplest and most generally satisfactory consisted of digestion with water, extraction with water and with alcohol, and drying in an inert gas.

1. *Digestion with Water.*—Crude rubber or latex was digested with water at an elevated temperature in an autoclave. The crude rubber, in lots of several kilograms, was sheeted thin and put into a Pyrex glass cylinder with sufficient water to cover it. The cylinder was placed in the autoclave in such a way that the rubber was not exposed to contamination by iron or copper salts from the autoclave or its fittings. Since the autoclave was heated by means of steam circulated through a jacket, a quantity of water was placed in the bottom of the autoclave to facilitate heat transfer to the Pyrex jar and its contents. Ammonia-preserved latex, when used instead of crude rubber, was placed in the Pyrex cylinder with no previous treatment other than straining. The autoclave was heated to about 190° C.,

which is the temperature of steam at a pressure of 167 pounds per square inch in excess of atmospheric pressure. The time of digestion was ordinarily three to four hours, exclusive of the time required for heating and cooling the heavy autoclave. The time and temperature of heating were probably in excess of that necessary to hydrolyze the proteins, but were employed in order to assure thorough penetration of the crude rubber by the water.

At the conclusion of the digestion, the water in which the rubber had been heated was dark colored and contained considerable organic matter. When latex was employed it was always found coagulated after digestion. A hand examination of the digested rubber indicated that the digestion process did not soften or degrade the rubber to any great extent.

2. *Washing with Water and Alcohol.*—The digested rubber was washed and extracted in order to remove protein-disintegration products, resins, sugars, soluble inorganic salts, and possible mechanical impurities. The washing and extraction were carried out with the use of an internal mixer of a type which was designed for the compounding of rubber.³ The mixing chamber was provided with a cover fitted with a reflux condenser to prevent the loss of solvent. The mastication of the rubber with the solvent in the internal mixer was a much more effective means of removing these various impurities than was percolation of the thinly sheeted material with the solvent in an extraction apparatus. The chief advantage of the internal mixer lay in the constant renewal of the surface of the rubber. This facilitated the removal of any mechanical impurities and pockets of solution, and probably accelerated greatly the extraction of substances slightly soluble in rubber. Furthermore, the use of the internal mixer obviated various difficulties which are attendant on the extraction of soft rubber in lots of several kilograms in an apparatus of the Soxhlet type.

The process of washing and extracting the digested rubber with water usually occupied 4 hours, during which time the water was changed every 15 or 30 minutes. Distilled water was used, and was kept vigorously boiling in order to exclude air and thus prevent oxidation of the rubber. At the end of the period the wash water was practically colorless and left only a very slight residue on evaporation.

Treatment with water was followed by a similar treatment with alcohol. For this purpose ethanol, containing not over 5 per cent of water and 10 per cent of methanol, was used. Alcohol was employed as a solvent for extracting the resinous components of rubber rather than acetone on account of its higher boiling point. When rubber was extracted with acetone at its boiling point, 56° C., a soft and almost pasty product was obtained on account of the mechanical working of the rubber at the relatively low temperature.

Extraction with alcohol was followed by a few minutes' extraction with one or two portions of boiling water in order to remove the alcohol. This was done because, in the subsequent drying, it seemed easier to remove the water than the alcohol. This point, however, was not investigated critically.

3. *Drying.*—The extracted rubber was dried by working it in the internal mixer at a temperature of 110° to 125° C. in an atmosphere of inert gas, usually nitrogen. A continuous stream of gas was passed through the mixer during the drying, which was ordinarily continued for about 30 minutes after steam had disappeared from the effluent gas.

III. Composition of the Purified Rubber

No extensive study was made of the composition of the purified rubber. Determinations of nitrogen, benzene-insoluble components, and ash were made on

representative preparations. Combustion analyses of high precision were made on two samples of the purified rubber.

1. *Nitrogen*.—Nitrogen was determined by the Kjeldahl method, using 2-gram samples of rubber. The results of analyses on rubber before and after purification are given in Table I. The nitrogen content of the original unpurified rubber was 0.3 to 0.6 per cent, while that of seven lots of the purified material ranged from 0.02 to 0.05 per cent, with an average value of about 0.03 per cent. The precision of the determination was of the order of 0.01 per cent.

2. *Ash*.—Determinations of ash were made by igniting 5-gram samples of rubber in crucibles of approximately 100-cc. capacity in an electrically heated muffle furnace, observing the usual precautions. In most cases an appreciable reduction in ash content resulted from purification. Only in the case of a sample of guayule rubber was there a small increase in percentage of ash. This may have resulted from the removal of a larger proportion of resins than of inorganic material in the purification process. The ash content of purified rubber made from clean plantation rubber or latex ranged from 0.04 to 0.24 per cent, with an average of about 0.12 per cent. Analyses made by ignition in a muffle and in a combustion furnace were in good agreement. Seven determinations on one preparation, by the former method, indicated an ash content of 0.15 ± 0.02 per cent, while five determinations by the latter method, which are reported in Table II, gave the result 0.13 ± 0.03 per cent.

3. *Benzene-Insoluble Components*.—The benzene-insoluble fraction of rubber was determined by dissolving 5-gram samples in 50 to 100 cc. of benzene to which about 1 gram of trichloroacetic acid had been added. On exposure to light for a few hours a limpid solution was obtained from which proteins, salts, and foreign materials, such as dirt or bark, could easily be separated by centrifuging. The residue was thoroughly washed with benzene and dried before it was weighed. The results which are given in Table I indicate that the original unpurified rubber contained from 2.5 to 5 per cent of insoluble material, and the purified rubber 0.1 to 0.3 per cent.

TABLE I
COMPOSITION OF RUBBER BEFORE AND AFTER PURIFICATION

Source of rubber	Preparation No.	Nitrogen		Benzene-Insoluble		Ash	
		Before Purification, %	After Purification, %	Before Purification, %	After Purification, %	Before Purification, %	After Purification, %
Smoked sheet	3	0.29	0.02	2.50	0.18	0.18	0.08
Guayule ^a	..	0.30	0.05	8.1	1.03	1.27
Pale crepe	6	0.31	0.02	0.16	0.14
	7	0.03
	8	0.03
	10	0.02	0.07
Latex-sprayed rubber	4	0.62	0.02	5.35	0.26	1.4	0.24
<i>Hevea</i> latex	11	0.02	0.04
	14	0.15
	19 ^b	0.004	0.33	0.19
	23 ^c	0.13	0.08
	27 ^c	0.31

^a The guayule rubber was digested with 4 per cent potassium hydroxide solution instead of water to destroy woody matter.

^b This sample of purified rubber was prepared by A. D. Cummings using the method of Cummings and Sebrell, *Ind. Eng. Chem.*, **21**, 553 (1929).

^c These samples were prepared and analyzed by A. D. Cummings.

4. *Carbon, Hydrogen, and Oxygen.*—Organic combustion analyses on three preparations of purified rubber were made with an apparatus capable of giving results of relatively high accuracy.⁴ The results are shown in Table II. The sums of the carbon, hydrogen, and ash found in the different analyses ranged from 99.82 to 100.06 per cent, with an average value of 99.95 per cent. Assuming the nitrogen content to be 0.03 per cent, the oxygen indicated by difference is only 0.02 per cent. This is evidence that practically all the resins and other non-hydrocarbon com-

TABLE II
COMBUSTION ANALYSES ON PURIFIED RUBBER

Source of rubber	Analysis No.	Carbon, %	Hydrogen, %	Ash, %	Total, %
Pale crepe	1	87.87	11.76	0.19	99.82
	2	87.75	11.95	0.25	99.95
	1	87.99	11.89	0.18	100.06
<i>Hevea</i> latex	2	88.05	11.87	0.10	100.02
	3	87.95	11.87	0.10	99.92
	4	87.94	11.85	0.15	99.94
	5	88.01	11.86	0.10	99.96
Calculated for C_5H_8		88.15	11.85	100.00

ponents were removed by the extraction process, and that the rubber did not suffer appreciable oxidation in the process of purification.

The data above do not warrant an exact statement of the purity of the rubber. If it is assumed, however, that the chief impurities are inorganic substances, proteins or their degradation products, and moisture, the sum of these is probably not in excess of 0.5 per cent, or the hydrocarbon content of the rubber may be estimated at about 99.5 per cent.

IV. Properties of the Purified Rubber

The purified rubber was dark in color, except when viewed in thin layers. The colored components were probably present in small amount and originated during the digestion with water at the high temperature.

No measurements were made of the consistency of the purified rubber. By hand examination it seemed to be comparable to or somewhat softer than crude rubber which had been thoroughly masticated or "broken down." The consistency was probably the result of the mechanical working accorded the rubber during the extraction and drying.

Determinations of the density and the refractive index were made on single samples of the purified rubber which had been prepared from latex. Dielectric constant, power factor, and conductivity measurements were made on all samples of the purified rubber.

1. *Density.*—The density of the purified rubber was determined at three temperatures with the use of a Pyrex glass pycnometer in which mercury was employed as the confining liquid.⁵ The density at 0° C. was 0.9209; at 20°, 0.9088; and at 61.2°, 0.8845. These values, when plotted against the temperature, lie on a straight line within probable experimental error, as is indicated by Fig. 1. The density at 25°, taken from the curve in this figure, is 0.9060. The coefficient of change in density with temperature is 0.000595 per degree, between 0° and 61.2°, or the density at any temperature, t , in this range is given by the relation:

$$d_t = 0.9060 + 0.000595 (25 - t)$$

By way of comparison the density of standard grades of commercial crude rubber at 25° C. is about 0.912, and the change in density per ° C. is 0.00062.⁶

2. *Refractive Index.*—The refractive index of the purified rubber for the *D* line of sodium was measured with an Abbé prism refractometer. Thin specimens suitable for measurement in this instrument were prepared by pressing out small sheets of rubber between layers of aluminum foil. These were applied to the prism and pressed against it so as to make optical contact without the use of a liquid. The temperature at which the determinations were made was controlled by circulating water around the prisms. The results which were obtained at temperatures from 7° to 43° C. are shown graphically in Fig. 1.

The refractive index of the purified rubber for the *D* line at 25° C., taken from the curve in Fig. 1, is 1.5184, which is approximately the same as the value 1.519

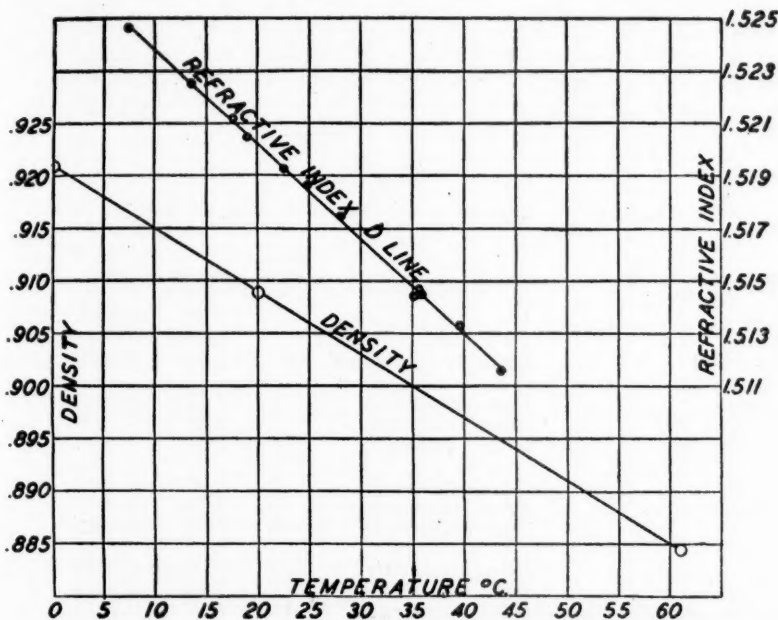


Figure 1—Density and Refractive Index of Purified Rubber

reported previously for crude rubber.⁷ The refractive index at temperatures other than 25° C. is given by the relation:

$$n_D' = 1.5184 + 0.00036 (25 - t)$$

The experimental results agree with the values indicated by this equation, with a maximum deviation of 0.0004 and an average deviation of 0.0001.

3. *Electrical Properties.*—Dielectric constant, power factor, and conductivity measurements were made on samples of purified rubber which had been prepared not only from wild and plantation *Hevea* rubber, but also from other natural rubbers of widely different botanical sources. The method of preparing test specimens and making electrical measurements is described fully elsewhere.⁸ The results of these measurements are summarized in Table III.⁹

The dielectric constant at 1000 cycles per second and 25° C. of all the samples of purified rubber which were examined was between 2.33 and 2.40, with an average value of 2.37. The dielectric constant of the unpurified rubber is higher and more

variable than this, ranging from 2.50 to 2.70 in most cases. The value, 2.37, probably approximates the dielectric constant of pure rubber hydrocarbon.

The power factor of purified rubber measured at 1000 cycles per second was less than that of rubber before purification, and ranged from 0.0008 to 0.0026, with an average value of 0.0015. This variability, in the light of general knowledge of power factor, may be attributed to residual impurities in the rubber, including moisture. The true power factor of rubber hydrocarbon is probably less than 0.0008, the lowest value found, because traces of most impurities are known to increase the power factor of hydrocarbons above the true value.

The conductivity of purified rubber, measured one minute after the application of potential, was decidedly lower and less variable than that of crude rubber. For different samples the conductivity ranged from 1.4 to 3.6×10^{-17} mho., with an average of 2.2×10^{-17} mho. As in the case of the power factor, the average conductivity is not to be regarded as the true conductivity of a hydrocarbon, since the effect of impurities is always to increase, never to decrease, the conductivity of the main component. Consequently, the conductivity of pure rubber hydrocarbon is in all probability smaller than the lowest value here reported.

TABLE III
ELECTRICAL PROPERTIES OF PURIFIED RUBBER AT 25° C.

Kind of Crude Rubber or Latex	Botanical Source	Preparation No.	Dielectric Constant ^a	Power Factor ^a	Conductivity, ^b Mho. $\times 10^{-17}$
Penang	<i>Ficus elastica</i>		2.39	0.0018	2.7
Guayule ^c	<i>Parthenium argentatum</i>		2.33	0.0011	3.7
Gaboon ball	Probably <i>Landolphia</i>		2.40	0.0013	3.3
Fine Para	<i>Hevea brasiliensis</i>	2	2.37	0.0008	1.6
Smoked sheet	<i>Hevea brasiliensis</i>	3	2.36	0.0008	1.6
Latex-sprayed	<i>Hevea brasiliensis</i>	4	2.35	0.0014	2.2
Pale crepe	<i>Hevea brasiliensis</i>	1	2.39	0.0010	1.7
	<i>Hevea brasiliensis</i>	6	2.36	0.0017	1.5
	<i>Hevea brasiliensis</i>	8	2.37	0.0016	1.9
Ammonia-preserved latex	<i>Hevea brasiliensis</i>	0	2.39	0.0018	2.2
	<i>Hevea brasiliensis</i>	11	2.36	0.0018	2.0
	<i>Hevea brasiliensis</i>	14	2.37	0.0014	2.6
	<i>Hevea brasiliensis</i>	27	2.39	0.0026	
	<i>Hevea brasiliensis</i>	31	2.41	0.0022	1.7
Average for all samples			2.37	0.0015	2.2

^a The dielectric constant and power factor were measured at a frequency of 1000 cycles per second.

^b The conductivity was measured one minute after the application of potential.

^c The purification of the guayule rubber used for these measurements included solution in benzene, filtration, and precipitation with acetone to effect the removal of woody impurities.

4. *Vulcanization Characteristics.*—No critical study was made of the vulcanization of purified rubber. Numerous samples, however, compounded with sulfur in proportions from 2 to 32 per cent by weight, exhibited a behavior on vulcanization that was apparently the same as that of similar mixtures of crude rubber and sulfur. When the samples were vulcanized from 20 to 40 hours at 140° C., the residual uncombined sulfur was less than 0.1 per cent in all cases except those where the total sulfur was 28 to 32 per cent. In the latter cases residual sulfur was present in varying proportions up to 0.8 per cent.

References

¹ The preparation of rubber hydrocarbon of high purity by the crystallization and distillation of rubber is the subject of a research being conducted by other investigators at this bureau. See *Technical News Bulletin of the Bureau of Standards*, No. 161, 85, September, 1930. Also, E. W. Washburn, "Crystalline Rubber Hydrocarbon," *Phys. Rev.*, **38**, 1790-1791 (1931).

² This method is similar to the one described by Kemp, *J. Franklin Inst.*, **211**, 44-47 (1931). The work here reported was done prior to the publication by Kemp. See *Technical News Bulletin of the Bureau of Standards*, No. 128, 2-3, December, 1927.

³ This internal mixer is described in *Technical News Bulletin of the Bureau of Standards*, No. 141, 1-2, January, 1929, and also in *India Rubber World*, **80**, No. 1, 78, April, 1929.

⁴ These analyses were made by H. J. Wing using the method described by Washburn, Bruun, and Hicks, *Bur. Standards J. Research*, **2**, 487 (1929).

⁵ The density determinations were made by A. D. Cummings.

⁶ A. T. McPherson, "Density of Rubber-Sulfur Compounds," *Bur. Standards Sci. Paper*, No. 560 (1927).

⁷ H. L. Curtis and A. T. McPherson, "Dielectric Constant, Power Factor, and Resistivity of Rubber and Gutta-Percha," *Bur. Standards Tech. Paper*, No. 299, 698 (1925). See also Shacklock, "Further Studies of Rubber Solutions," *Trans. Inst. Rubber Ind.*, **7**, 356 (1932).

⁸ H. L. Curtis, A. H. Scott, and A. T. McPherson, "Properties of the System: Rubber-Sulfur. Part III. Effect of Temperature and Frequency on the Dielectric Constant, Power Factor, and Conductivity." In preparation.

⁹ The electrical measurements were made by A. H. Scott.

NATURAL AND SYNTHETIC RUBBER. IX. THE PRODUCTS OF DESTRUCTIVE DISTILLATION OF EBONITE

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND ALVIN F. SHEPARD

Introduction

It has been shown that there is a definite relationship¹ between the rubber molecule and its pyrolysis products, and consequently the thermal decomposition of ebonite has been undertaken to throw light on the nature of the rubber sulfur complex.

It was relatively simple to correlate the pyrolysis products of raw rubber with the formula of the parent molecule, as the rubber formula had been previously established by oxidation. However, the formula of ebonite is still unknown, and cannot be arrived at by ordinary methods, because ebonite is amorphous, insoluble, non-volatile, completely saturated, and inert toward chemical agents. A correlation of its pyrolysis products may thus be the only way of establishing its formula.

The pyrolysis products of ebonite, the decomposition products of a mixture of rubber and sulfur, and the interaction of sulfur and the pyrolysis products of raw rubber have been investigated to establish a basis from which the formula of ebonite may be derived.

The present paper presents the study of the products obtained when ebonite is destructively distilled.

Procedure.—Thirty-six kilograms of ebonite were destructively distilled in the manner reported previously. The volatile products were progressively condensed by means of warm water, ice water and solid carbon dioxide. The non-condensed gases were washed through a copper sulfate solution to eliminate hydrogen sulfide, and finally led through another condenser cooled with carbon dioxide. The condensed products were subjected to fractional distillation, and from the various cuts thus obtained the thiophene homologs were separated by mercuration.

Results.—The amount of hydrogen sulfide liberated during pyrolysis accounted for approximately one-half of the sulfur originally present in the ebonite. As a consequence, the oils obtained were of a highly unsaturated character. An examination of the oils boiling below 170° established the presence of mercaptans, sulfides, thiophene homologs and *m*-xylene. The examination failed to detect disulfides. The oils boiling above 170° were rich in sulfur; they were not further investigated. The

¹ Midgley and Henne, *THIS JOURNAL*, 51, 1215 (1931).

limited stability of a portion of the sulfur compounds precluded their separation, and hence the determination of their constitution. The thiophenes and the hydrocarbons were stable enough to be successfully investigated, and it was thus possible to isolate and identify 2-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene, 2,5-methylethylthiophene and *m*-xylene. At the same time it was shown that benzene, toluene, thiophene, 2,5-dimethylthiophene, 2,3-methylethylthiophene or trimethylthiophenes were not present in significant quantities. Similarly, the absence of other isomers of the thiophene homologs was established. The yields were: thiophenes, 1%; xylene, 0.1%, of the total quantity of ebonite used.

Experimental Part

The ebonite used in this investigation was prepared by the Inland Manufacturing Company of Dayton, Ohio, through the kindness of Dr. A. H. Flower, to whom we here wish to express our thanks. The following mix was used: first latex crepe, 100, sulfur, 32, diphenylguanidine, 2, "Kadox," 2, stearic acid, 2. The mix was cured for eight hours at 148°; analysis showed 0.1% free sulfur at the end of this time.²

Thirty-six kilograms of this ebonite were cracked as previously described. The vapors were progressively condensed at 100, 0 and -80°. The condensate obtained at -80° was chiefly hydrogen sulfide and quite free of hydrocarbons boiling below 30°. A rough estimate of the amount of hydrogen sulfide liberated was made by passing the cracked gases through copper sulfate solutions. Table I summarizes the results.

TABLE I

	Liquid	H ₂ S	Water	Coke	Uncondensed gases and loss
Yield on ebonite, %.....	59	13	4	6	18

The liquid was topped to 200°. The higher boiling materials contained 14.2% sulfur; they were not further investigated. The distillate below 200° (3600 g. or 10% of the original liquid) was systematically fractionated. After three runs, the material boiling below 120° was repeatedly washed with alkali to remove mercaptans completely, and the fractionation was resumed and carried out to its practical limit. Table II shows the results of the final fractionation together with the physical properties and sulfur content of the fractions. Double bond determinations were made only on the fractions containing little sulfur.

² The effect of the ingredients other than sulfur and rubber in the ebonite may be discounted, as shown by the following experiments. A small batch of ebonite, prepared from a crepe rubber-sulfur mix containing 32% sulfur and no accelerators, was destructively distilled. In the distillate, 2-methylthiophene, 2,3-dimethylthiophene and *m*-xylene were positively identified. Thiophene, benzene, toluene, 3-methylthiophene and *p*-ethyltoluene were absent, while 2,4-dimethylthiophene and 2-ethyl-5-methylthiophene appeared to be present, although they were not positively identified. An ebonite was also prepared from sodium-rubber containing 32% sulfur and no accelerators. The pyrolysis products of this sodium rubber ebonite were also quite similar to those from crepe rubber ebonite. The mercuration treatment allowed the recovery of small amounts of thiophene homologs, similar in their indophenin reactions to those obtained from the crepe rubber ebonite.

TABLE II

Temp., °C.	Volume, cc.	dV/dT	d_{44}^{20}	n_D^{20}	Δ	S, %
30-36	14	2	0.672	1.389	0.9	
36-40	8	2	.675	1.400	.9	
40-51	6	0.5		1.399	.8	1.1
51-57	12	2	.702	1.392	.6	2.1
57-61	22	5	.704	1.393	.7	1.7
61-65	13	3	.714	1.400	.7	1.1
65-69	26	7	.725	1.413	.9	1.3
69-73	22	5	.743	1.425	1.0	1.5
73-77	12	3	.770	1.436	0.9	2.2
77-80	12	4	.761	1.429	.8	1.9
80-88	17	2	.755	1.416	.6	1.7
88-90	15	8	.742	1.410	.7	1.0
90-94	21	5	.739	1.413	.8	0.6
94-96	18	9	.741	1.416		
96-105	22	2	.797	1.441		
105-107	23	12	.847	1.461		
107-109	54	27	.867	1.468		13.0
109-111	125	63	.873	1.471		14.5
111-113	55	28	.856	1.464		13.5
113-119	28	5	.835	1.454		9.1
119-125	30	5	.813	1.446		7.4
125-130	33	7	.843	1.457		11.4
130-134	40	10	.861	1.467		13.9
134-136	26	13	.873	1.472		14.0
136-138	111	56	.894	1.485		14.5
138-140	194	97	.909	1.490		15.4
140-142	39	20	.916	1.491		16.8
142-145	20	7	.905	1.488		16.2
145-151	15	3	.887	1.482		14.5
151-156	25	5	.884	1.480		14.6
156-159	55	18	.906	1.487		18.3
159-160	129	129	.920	1.494		
160.0-160.5	125	250	.929	1.497		
160.5-161.5	125	125	.935	1.500		19.6
161.5-162.7	100	83	.938	1.502		Composite sample
162.7-165.0	120	52	.936	1.504		
165-169	100	25	.935	1.505		
169-172	100	33	.926	1.501		
172-175	100	33	.919	1.497		
175-180	100	20	.919	1.495		17.3

Each of the three main fractions, b. p. 109-111°, 138-140° and 160-160.5°, was a complex mixture. Distillation from aniline separated these mixtures roughly into hydrocarbon-rich fractions and sulfur-rich fractions, but since this was insufficient, chemical methods were preferred.

Mercaptans and Disulfides.—A mercaptan concentrate was isolated by steam distilling the alkali washings of the ebonite fraction boiling below 120°. It weighed only 8 g. and boiled chiefly from 66-80°. It had the characteristic mercaptan odor and gave typical mercaptan reactions with iodine, alcoholic lead acetate, sodium plumbite and

mercuric oxide. The ebonite fractions boiling from 100–180° contained mere traces of mercaptans.

Disulfides were absent from the ebonite fractions boiling below 170°; this was shown by the failure to form mercaptans on reduction with zinc and glacial acetic acid.³

Thiophenes and Aromatic Hydrocarbons.—Thiophene and its lower homologs are very readily mercurated.⁴ Thiophene is quantitatively extracted from benzene⁵ by a boiling solution of mercuric acetate in dilute acetic acid; it forms a di-mercuri compound, and is readily regenerated from this compound by boiling hydrochloric acid. The various ebonite fractions were refluxed for thirty minutes or more with Dimroth's reagent (40 g. mercuric oxide), 40 cc. glacial acetic acid and 200 cc. water) and subjected to steam distillation. This operation removed unreacted aromatic and saturated hydrocarbons and left behind a complex mixture, from which the thiophenes were regenerated in a fair state of purity by boiling hydrobromic acid. The mercuric acetate treatment always caused the loss of the olefins and of up to 70% of the sulfur compounds. In order to show that this loss of sulfur derivatives was not due to the preferential destruction of some definite thiophene homolog, the mercuration and regeneration of thiophene, 2-methylthiophene, and of 3-methylthiophene were checked. None was appreciably oxidized; all were completely regenerated from their mercury compounds by hydrobromic acid. This check was regarded as important because Volhard reports that 2,5-dichloromercuri-3-methylthiophene is very difficult to split with acids.

Other Sulfur Compounds.—Many unsuccessful attempts were made to isolate by other methods the sulfur compounds lost in the mercuration procedure. Significant are the following observations.

Fractions containing these sulfur compounds react with mercurous nitrate monohydrate, a reagent used by Faragher, Morrell and Monroe³ for the quantitative removal of sulfides from thiophene and hydrocarbons.

Diethyl sulfide may be recovered from its mixture with a hydrocarbon and thiophene by shaking with a solution of mercuric acetate and steam distilling the mercuric acetate solution but no sulfur compound is recoverable from the 109–113° cuts in this way.

The ebonite distillates did not react appreciably with dimethyl sulfate, a reagent which reacts with dimethyl sulfide on gentle warming.

The early experiments with aniline fractionation showed that in the case of the large fractions boiling at 107–113°, 136–142° and 159–165°, the sulfur compounds lost had physical properties not widely different from the thiophenes with which they were associated.

A proposed explanation is that the lost sulfur compounds represent members of an homologous series of dihydrothiophenes.

Tests for Individual Compounds.—The mercuration procedure was systematically applied to all the ebonite distillates boiling in the range 60–165°. Unless otherwise stated, all mercury derivatives were prepared and purified exactly according to the directions of Steinkopf.^{4a,b}

Thiophene and Benzene.—One drop of oil was recovered from the mercury compounds obtained from the ebonite fractions boiling from 66–88°. This drop did not give the indophenin reaction; thiophene was therefore absent. The steam distillate from the mercury compounds was treated with bromine water and steam distilled; 1 cc. of

³ Faragher, Morrell and Monroe, *Ind. Eng. Chem.*, **19**, 1281 (1927).

⁴ Volhard, *Ann.*, **267**, 172 (1892); Steinkopf and Bauermeister, *ibid.*, **403**, 50–72 (1914); (a) Steinkopf, *ibid.*, **413**, 310–333 (1917); (b) **424**, 23–61 (1921); (c) **428**, 138 (1922).

⁵ Dimroth, *Ber.*, **32**, 759 (1899).

an oil was obtained. Nitration to dinitrobenzene was attempted but none could be isolated.

2-Methylthiophene.—The product isolated boiled at 111.5–112.5° (741 mm.), and had d_4^{20} 1.017, n_D^{20} 1.5132, molecular refraction observed 29.0, theoretical 30.1. It gave the green indophenin reaction characteristic of 2-methylthiophene. The following derivatives were prepared: 5-chloromercuri-2-methylthiophene, m. p. 204°, alone and in a mixture with authentic material; 2-methylthiophene-5-mercurothiocyanate, m. p. 200–201° (decomp.); tribromo-2-methylthiophene, m. p. 83°. Steinkopf^{4b} gives the melting points of the first two derivatives as 204° and 202–204° (decomp.), respectively. Gattermann, Kaiser and Meyer⁶ give a melting point of 86° for tribromo-2-methylthiophene and state that a mixture of the 2- and the 3-isomers is inseparable by crystallization and melts at 74°. Comparison of the relative amounts of alcohol-insoluble material formed on mercurating the thiophene from ebonite and synthetic 3-methylthiophene indicated⁷ that less than 10% of 3-methylthiophene could have been present in the ebonite product.

Toluene.—The steam distillate containing the toluene was brominated at 0° with bromine water and steam distilled to separate the unreacted constituents from olefin bromides. After washing with sulfuric acid the product boiled at 109.5–111.5° and had n_D^{20} 1.4812. A saturated compound was present with the toluene since the material was not completely soluble in 10% oleum. Nitration gave dinitrotoluene of m. p. 69–70° alone and in a mixture with authentic material. A check experiment showed that no significant amount of toluene could have been mercurated and thus lost in the procedure of separation.

Dimethylthiophenes.—The thioxene mixture as isolated boiled at 139.5–141.5° (745 mm.) corr. and had n_D^{20} 1.5137 and d_4^{20} 0.984. Mercuration with mercuric chloride according to Steinkopf's procedure yielded a product completely soluble in benzene or alcohol. This shows the absence of 3,4-dimethyl- or 3-ethylthiophene;^{4c} Steinkopf states that these isomers form di-mercuri compounds insoluble in these or other low-boiling solvents. The boiling point of the mixture is too high to be compatible with the presence of any significant quantity of 2-ethylthiophene (b. p. 132–134° corr.).⁸

Fractional crystallization of the mercury chloride compounds of the ebonite thioxenes from benzene permitted the isolation of 50% of the mercury compounds as 5-chloromercuri-2,3-dimethylthiophene, m. p. 217.5–218.5° (decomp.) alone and in a mixture with authentic material. This substance was converted to 2,3-dimethylthiophene-5-mercurothiocyanate,^{4b} which shrunk and blackened at about 198° and did not melt up to 240°. Steinkopf states that this compound darkens at 200–202° and does not melt below 240°. Further confirmation of the presence of 2,3-dimethylthiophene was obtained by permanganate oxidation of the original thioxene mixture. A mixture of mono- and dicarboxylic acids resulted and the mono acid was steam distilled out from a very concentrated solution. Recrystallized twice from water it melted at 140–141° and its melting point was raised by mixture with the acid of m. p. 143° obtained similarly from the oxidation of synthetic 2,3-dimethylthiophene. The dicarboxylic acids gave the fluorescein reaction strongly.

Anal. of monocarboxylic acid: (a) from synthetic 2,3-dimethylthiophene; C, 50.8, 50.9; H, 4.1, 4.2. Calcd. for $C_6H_4O_2S$: C, 50.7; H, 4.3. (b) From ebonite thioxene: molecular weight by alkali titration, 141.5; calcd. for $C_6H_4O_2S$, 142.

The other mercury compounds occurring with 5-chloromercuri-2,3-dimethylthiophene were much more soluble in all solvents, melted mostly at 135–150°, and could not

⁶ Gattermann, Kaiser and Meyer, *Ber.*, 18, 3009 (1885).

⁷ Later experiments have shown that 3-methylthiophene is readily formed by the interaction of isoprene and boiling sulfur.

⁸ Meyer and Kreis, *Ber.*, 17, 1560 (1884).

be purified satisfactorily by crystallization. Steinkopf has noted a considerable difference in the rates at which the substituted thiophenes mercurate, and a separation of 2,4-dimethylthiophene derivatives was accomplished by the application of this principle. The above-mentioned mixture of mercury compounds was converted to the thioxenes with hydrogen bromide and the thioxenes were remercurated. After five minutes the mercury compound formed was separated from the mercuration mixture and reconverted to the thioxenes. The mercuration was then repeated, and after two minutes the formed mercury compound was again removed. The final amount of this mercury compound corresponded to 10% of the original mixture of mercury compounds obtained from the ebonite thioxenes. Crystallized from benzene, it melted at 168–169° in a bath preheated to 165°; on slower heating it sintered together somewhat above 170° but did not melt. The mercuric chloride addition product of oxodihydromercuri-2,3-dimethylthiophene is stated by Steinkopf⁹ to melt at 167–168° on rapid heating; slow heating causes only a gradual sintering together. From this compound were prepared 5-chloromercuri-2,4-dimethylthiophene, m. p. 137.5–138.5°; 2,4-dimethylthiophene-mercurithiocyanate, m. p. 175–177° (sinters at 173°); and 5,5'-mercuri-bis-2,4-dimethylthiophene, m. p. 160–161° (with sintering). Steinkopf gives the melting points of these substances as 138–139°, 173–175° (sinters at 171°) and 160–161° (with sintering), respectively. The presence of 2,4-dimethylthiophene in the ebonite distillates is thus proved.

An attempt was made to isolate 2,5-dimethylthiophene by a similar method based on the principle that the compound mercurates much more slowly than the 2,3- and 2,4-isomers. None was found.

***m*-Xylene.**—The xylene fraction was separated from olefins in the same way as the toluene. The product had b. p. 138–139° (746 mm.) (corr.), d_4^{20} 0.852 and n_D^{20} 1.4895. Sulfonation with oleum left about 10% of saturated hydrocarbon. According to Timmermans⁹ *m*-xylene has b. p. 139.3° (760 mm.) and d_4^{20} 0.8641. Ten drops of the xylene fraction was added to 10 cc. of concentrated sulfuric acid and 5 cc. of fuming nitric acid; the mixture was boiled for two minutes, then poured on ice and diluted with water. The precipitate was filtered off, washed with water and then with 15 cc. of cold 50% alcohol. The dried product showed m. p. 177–179°; after one crystallization from 50% alcohol it melted at 181–182° alone and in a mixture with authentic material. This proves the presence of *m*-xylene, substantially free of isomers.

2-Methyl-5-ethylthiophene.—The product first recovered from the mercuration procedure still contained unsaturated compounds and had d_4^{20} 0.957. To eliminate the unsaturated material the procedure of mercuration and regeneration was repeated. The product thus obtained boiled at 159.8–161.3° (chiefly 160.1–160.6°), had a freezing point –74.2°, d_4^{20} 0.958, n_D^{20} 1.5048 and a mol. wt., as determined by the freezing point depression in benzene, of 124.2, 126.5.

Anal. Calcd. for $C_7H_{10}S$: S, 25.42. Found: S, 24.05, 24.10, 23.90.

A specimen was prepared from the mercury acetate compound crystallized from glacial acetic acid; this preparation boiled at 159.5–160.6°, had a freezing point of –69.4°, d_4^{20} 0.9644, n_D^{20} 1.5063, and contained 25.28, 25.31% S. Presumably the earlier preparation still contained a small amount of hydrocarbon.

Synthetic 2-methyl-5-ethylthiophene boils at 159.8–160.4° and has¹⁰ the freezing point –68.4°, d_4^{20} 0.9663 and n_D^{20} 1.5073. The freezing point of the product from ebonite (f. p. –74.2°) was raised by admixture with the synthetic material. It is noteworthy that this 2,5-disubstituted thiophene mercurates more slowly than the other compounds heretofore described, a behavior which parallels that reported by Steinkopf

⁹ Timmermans, *J. chim. phys.*, 27, 2 (1930).

¹⁰ The preparation and physical properties of the synthetic specimen are described in a separate paper now submitted for publication in THIS JOURNAL.

for 2,5-dimethylthiophene. Both synthetic 2-methyl-5-ethylthiophene and the product from ebonite (f. p. -74.2°) gave an intense red-brown color when added to a solution of isatin in commercial sulfuric acid. Dr. W. R. Brode has very kindly compared the absorption spectra of both these colorations with a spectrophotometer, and has found no difference whatever in the spectra.

It is evident that the material from ebonite is 2-methyl-5-ethylthiophene, reasonably free from isomers.

A trimethylthiophene, especially the 2,3,5-isomer, might be expected to mercurate with extreme difficulty, and these compounds were sought in the steam distillate from the mercuration. Youtz and Perkins¹¹ state that 2,3,5-trimethylthiophene dissolves in sulfuric acid and is reprecipitated apparently unchanged on dilution. Schulze¹² has recovered thiophene and its homologs by diluting with water and steam distilling the sulfuric acid washings of various aromatic hydrocarbons obtained from coal tar. Accordingly, the steam distillate from the mercuration of the ebonite fractions boiling in the neighborhood of 160° was carefully washed, cold, with 2 volumes of concd. sulfuric acid. The sulfuric acid extract was drawn off and ice and water were added to it, which caused the separation of an oil. The oil was removed, steam distilled, and then distilled over sodium. There was thus recovered 2 g. of a product of b. p. $158-168^{\circ}$ which had n_D^{30} 1.484. A measurement of the depressions of the freezing point of 2-methyl-2-ethylthiophene caused by the addition of this material and of *n*-nonane was made. This measurement showed that at least 50% of the material recovered by sulfuric acid treatment was 2-methyl-5-ethylthiophene, which fact, in view of the low refractive index of the material, shows the practical absence of trimethylthiophenes.

Aromatic hydrocarbons were present only in insignificant amount in the ebonite fractions boiling from $156-165^{\circ}$, since less than 1 g. of hydrocarbon (b. p. $160-163^{\circ}$, n_D^{30} 1.472) was recovered from the sulfuric acid washing of the steam distillates.

TABLE III
AMOUNTS OF PRODUCTS RECOVERED BY PYROLYSIS OF 36,000 G. OF EBONITE

Compound	Recovered, g.	Compound	Recovered, g.
Benzene	<0.5	2,4-Dimethylthiophene	10
2-Methylthiophene	10	<i>m</i> -Xylene	50
Toluene	1	Aromatic hydrocarbon, b. p.	
2,3-Dimethylthiophene	50	ca. 160°	<1
		2-Methyl-5-ethylthiophene	240

Summary

The following compounds have been identified in the products obtained from ebonite by destructive distillation: 2-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene, 2,5-methylethylthiophene and *m*-xylene. These results will be used to derive the structural formula of ebonite.

¹¹ Youtz and Perkins, *THIS JOURNAL*, 51, 3511-3516 (1929).

¹² Schulze, *Ber.*, 18, 497 (1885).

NATURAL AND SYNTHETIC RUBBER. X. CONSTITUENTS OF THE RUBBER HYDROCARBON

By THOMAS MIDGLEY, JR., ALBERT L. HENNE AND MARY W. RENOLL

It has been shown in the seventh paper of this series,¹ that nitrogen-free rubber hydrocarbon can be prepared by fractional precipitation of natural rubber from a mixture of alcohol and benzene. This fractionation method is now applied to the rubber hydrocarbon itself to determine whether it is a single individual or a mixture of various components, and, in the last event, to isolate these constituents.

Some criterion is needed to follow the progress of any fractionation. The measurement of a well-defined physical property is best. In the present research, use is made of a standardized precipitation point (abbreviated to s. p. p. in the text), which is defined as follows. The standard precipitation point of a rubber specimen is the temperature at which a sudden increase of turbidity occurs in a slowly cooled solution of 0.85% rubber, 28.55% absolute alcohol and 70.60% benzene. The manner in which the s. p. p. is determined is described in the experimental part of this paper.

Procedure

Two hundred and fifty grams of crepe rubber was dissolved in benzene and fractionated into primary cuts. The method of fractionation was a duplication of that reported in the seventh paper. The technique, however, was improved to prevent alteration of the specimen by light or oxygen. The flasks containing the rubber solutions were always completely covered with black cloth, frequently evacuated and filled with carbon dioxide. The solvents were removed by suction at room temperature. The rubber samples were stored in a bed of solid carbon dioxide. They were allowed to reach room temperature and exposed to atmospheric oxygen only during the short time required to take a sample for s. p. p. determinations.

Table I reports the results of this primary fractionation.

The tabulated results are shown on the chart, where the percentages are plotted against the s. p. p. They are represented by the solid line: the length of the horizontal lines measures the size of the fractions from A₁ to A₆, in percentage of recovered rubber. Fraction B could not be shown on the chart since its s. p. p. could not be determined. It amounted to 18.6% of the total, and consequently the curve on the chart stops short of 100% by this amount, *viz.*, at 81.4%.

Each of the primary cuts, from A₁ to A₆ inclusive, amounting to 81.5% of the rubber recovered, was then resubjected to the same fractionation

¹ Midgley, Henne and Renoll, *THIS JOURNAL*, 53, 2733 (1931).

TABLE I
PRIMARY FRACTIONATION OF 250 G. OF CREPE RUBBER

Fractions	Amount, g.	Standard precipitation point (s. p. p.)	% based on 233.6 g.	
A ₁	44.8	33.0°	19.2	81.5%
A ₂	38.8	33.0°	16.6	
A ₃	46.5	34.9°	19.9	
A ₄	28.2	35.0°	12.1	
A ₅	31.9	35.3°	13.7	
B	43.4	Not obtained	18.6	
Total	233.6		100.1%	
Loss	16.4			

The loss of rubber during this separation amounts to 6.6% of the original 250-g. sample. This 16.4-g. loss includes an estimated amount of 12.5 g. of so-called "resins."

TABLE II
SECONDARY FRACTIONATION OF FRACTIONS A₁ TO A₅, *vis.*, 81.6% OF THE RUBBER
HYDROCARBON

Fractions	Amounts, g.	S. p. p.	% based on 190.2 g. = 81.5%
A ₁ Top ^a	11.0	32.1	5.4
Bottom ^a	29.8	34.2	14.7
A ₂ Top	9.8	32.5	4.8
Bottom	24.2	34.2	11.9
A ₃ Top	6.7	31.2	3.3
Bottom	30.7	34.8	15.1
A ₄ Top	4.2	31.2	2.1
Bottom	19.7	35.0	9.7
A ₅ Top	3.8	31.5	1.9
Bottom	25.7	35.1	12.6
Total	165.6		81.5
Loss	24.6		

The losses are almost entirely due to sampling for s. p. p. determinations.

^a "Bottom" is the rubber which settles out from a benzene-alcohol mixture held at 1° below its precipitation point. "Top" is the rubber chilled out from the supernatant liquid.

method. The only experimental detail altered was the lengthening of the time allowed for complete separation, to fourteen hours. The results are given in Table II. These results appear on the chart.

A third fractionation was then accomplished as follows. Cuts with an s. p. p. lower than 33° were put together, while cuts with an s. p. p. higher than 33° were united. The two fractions thus formed were separately fractionated as for the secondary fractionation, and the results shown in Table III were obtained. These results appear on the chart.

The third fractionation is only slightly better than the second one.

It indicates that more than 50% of the initial material is no longer fractionated, *viz.*, the cut with an s. p. of 35°.

Since small amounts of the lower fractions were lost by solubility in the alcohol-benzene mixture, it was decided to investigate this lower portion by a somewhat modified technique.

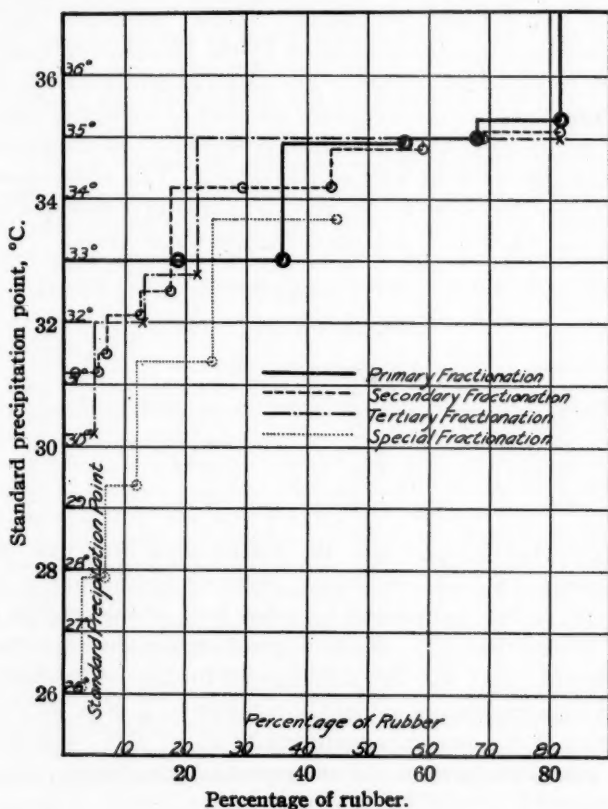


Fig. 1.

TABLE III

TERTIARY FRACTIONATION OF FRACTIONS A₁ TO A₄, OR 81.6% OF RUBBER HYDROCARBON

Fractions		Amounts, g.	S. p. p.	% based on 190.2 g. = 81.5%
Sum of tops	{ Top	8.5	30.2	4.7
	{ Bottom	15.7	32.8	8.8
Sum of bottoms	{ Top	14.4	32.0	8.1
	{ Bottom	107.3	35.0	59.9
Total		145.9		81.5
Loss		19.7		

The losses are almost entirely due to sampling.

A solution containing two hundred and fifty grams of crepe rubber was prepared and therefrom fractions A₁ and A₂ were obtained as before. After discarding the remainder of the rubber, these two fractions, A₁ and A₂, were redissolved in their original solvent, thus avoiding the loss of portions which were so soluble in the alcohol-benzene mixture that they could not be completely precipitated by chilling. These combined fractions were then treated by a procedure identical to the primary fractionation, and a fraction B₁ collected and stored. The supernatant liquid was then chilled. This precipitated some more rubber; one-half of the chilled liquid was then decanted and discarded. The chilled precipitate was then redissolved by warming in the retained half of the liquid. The whole procedure was repeated to give fractions B₂, B₃, etc. The results of this special fractionation are listed in Table IV and represented on the diagram.

TABLE IV
SPECIAL FRACTIONATION

Fractions	Amounts, g.	S. p. p.	% based on a total of 233 g. as 100%
B ₁	48.4	33.7	20.7
B ₂	29.2	31.4	12.5
B ₃	12.0	29.4	5.1
B ₄	9.4	27.9	4.0
B ₅	6.5	26.1	2.8

Results.—The diagram and the tables show that the present procedure separated a single component, characterized by an s. p. p. of 35.0%. The amount of this component exceeded 55% of the original rubber. A quantity of less than 20% of the original rubber was separated as a less soluble fraction, and was not investigated further; it probably still contained an appreciable amount of the component s. p. p. 35°. The highly soluble part of the rubber, amounting to about 25%, was fractionated; it failed to reveal the presence of an important constituent, except more of the component s. p. p. 35°.

There was quite a difference in appearance between the high and low s. p. p. fractions. The rubber of s. p. p. 35.0° was very tough, non-tacky, and somewhat opaque. The lower fractions were soft, but white in color, showing no apparent signs of oxidation. The insoluble portion was yellow, in its fresh state, and darkened on standing. It had little elasticity and resembled horn more than rubber.

Conclusion.—It is therefore concluded that the original rubber specimen consisted of, (1) a soluble portion containing several individuals and totaling more than 20% of the specimen, (2) a single soluble component present in excess of 50% of the total, and (3) an insoluble portion amounting to less than 20% of the total.

Discussion.—The origin of the more soluble portions of rubber is

obscure. Staudinger² suggests the possibility of forming such a portion by partial oxidation of the original molecule. Since precautions were taken to avoid oxidation during the course of the fractionation, it is suggested that the more soluble fractions were generated during the washing and sheeting of the original coagulate.

The present results bear a definite relation to two controversial points.

(1) Staudinger² has advanced the view that rubber is made up of a series of polymer homologs of many different lengths. It is now shown that though such a series may exist, to a limited extent, in the more soluble portions of rubber, the main constituent is one definite polymer.

(2) It is generally felt that in order to obtain a good grade of soft rubber goods, a two-phase system is required, implying that both sol and gel rubber should be present. Sol rubber, separated from gel, has been satisfactorily vulcanized, but the completeness of the separation was questioned. It is now found that pure sol rubber of s. p. p. 35° does give a satisfactorily vulcanized material (500% elongation and 4100 lb. tensile strength). That this sol rubber is of high purity is practically certain.

Experimental

Determination of the Standard Precipitation Point.—A 1.288-g. sample of the rubber (free from solvent) is placed in a 250-cc. Erlenmeyer flask. One hundred cc. of c. p. benzene is added. The flask is set away in the dark, under carbon dioxide, until complete solution is obtained. To this solution, warmed to about 50°, is added a hot mixture of 27 cc. of benzene and 56 cc. of absolute alcohol, and the whole is stirred and intermittently warmed until entirely clear. A calibrated thermometer reading tenth degrees is placed in it and it is allowed to cool. When the mixture becomes suddenly turbid, the temperature is read. This is the experimental precipitation point. It is reproducible to $\pm 0.1^\circ$. After checking the point, the flask is equipped with a bent tube carrying a water jacket on its downward branch. This branch delivers into a 250-cc. receiver cooled in ice; the receiver is in turn connected to a second one cooled in a mixture of carbonic snow and acetone, to ensure the recovery of all solvents during distillation. Atmospheric moisture is kept out of the system by means of a calcium chloride tube. While passing a slow stream of purified carbon dioxide through the system, the solvents are distilled with a steam-bath. The distillate is weighed, and its refractive index is measured in a Pulfrich refractometer, at 20.0°. From a previously constructed curve, the composition of the distillate is read. The rubber sample is weighed as soon as the distillation is finished, and its increase in weight, regarded as benzene, is added to the amount of benzene in the distillate. The percentages of alcohol and benzene are thus determined with accuracy; they can be duplicated to 0.1%. By means of the chart, Fig. 2, paper VII, the experimental precipitation point is then corrected to standard conditions, *vis.*, 28.55% alcohol and 0.85% rubber. This is the s. p. p. Including experimental errors and corrections, the s. p. p. determination is correct within $\pm 0.2^\circ$.

Summary

1. Fractional precipitation has been used to determine and isolate the constituents of the rubber hydrocarbon.

² Staudinger and Bondy, *Ann.*, [2] 488, 153 (1931).

2. A "standard precipitation point" has been devised and its use advanced as a physical constant of rubber.

3. The presence of a single component, amounting to more than 50% and characterized by a standard precipitation point of 35°, has been demonstrated.

4. The presence of highly soluble portions, of indeterminate s. p. p., has been shown.

COLUMBUS, OHIO.

NATURAL AND SYNTHETIC RUBBER. XI. CONSTITUENTS OF THE MILLED RUBBER HYDROCARBON

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND MARY W. RENOLL

The tenth paper of this series¹ has shown that *unmilled* pale crepe rubber contains a single "sol" component, which constitutes more than one-half of the specimen, and a continuous series of undefined "sol" portions amounting to about 20% of the specimen. These results have been obtained by a fractional precipitation from a benzene-alcohol mixture.

The same method of investigation has now been applied to *thoroughly milled* pale crepe rubber, and the present paper shows that the whole specimen is made up of a continuous series of undefined "sol" components, in undefined proportions.

Procedure.—Pale crepe rubber was milled for one hour on cold rolls. A 250-g. specimen was dissolved in benzene, and fractionated into primary cuts, by the method described.¹ Although the principle of fractionation remained unchanged, minor experimental details were altered, as follows.

Milled rubber is much more soluble in a given benzene-alcohol mixture than unmilled rubber. To illustrate: the s. p. p.'s¹ of the rubber specimen used, before and after milling, were 35.4 and 27.7°, respectively. Consequently, in order to be able to carry out the fractionation at a convenient temperature, *vis.*, about 40°, the solvent was made richer in alcohol than previously reported. In all cases, the length of time allowed for separation was extended to fourteen hours. Chilling out was accomplished by letting the solutions stand (under vacuum) in a refrigerator at about -10° for six hours. Since the fractions obtained from milled rubber did not precipitate sharply from an alcohol-benzene mixture, the experimental precipitation point could not be duplicated closer than ±0.2°.

Table I shows the results of the primary fractionation.

TABLE I
PRIMARY FRACTIONATION OF 250 G. OF MILLED CREPE RUBBER

Fractions	Amounts, g.	Standard precipitation point (s. p. p.) in degrees	% based on 233.4 g.	
A ₀	36.4	23.2	15.6	81.2
A ₁	66.4	23.4	28.4	
A ₂	68.5	24.3	29.3	
A ₃	30.3	24.9	13.0	
A ₄	24.5	24.9	10.5	
B	7.3	Not obtained	3.1	
Total	233.4		99.9	
Losses	16.6			

Fractions A₁ to B inclusive were obtained by the previously described method of operation.

¹ Midgley, Henne and Renoll, *THIS JOURNAL*, 54, 3343 (1932).

Fraction A_0 was found in the supernatant liquid remaining after the separation of A_1 , in the following manner: the liquid was cooled to -10° and kept at that temperature until the lower half of the mixture (containing the rubber and benzene) had frozen. The upper half containing the so-called "resins" was decanted, and the rubber was precipitated from the benzene of the lower half with acetone.

The reported losses include an estimated amount of 12.5 g. of "resins," soluble in alcohol. Hence the actual losses amount only to 4 g., viz., about 1.5%.

The tabulated results appear on the chart, where the percentages of rubber are plotted against the s. p. p. They are represented by the solid line. The length of the abscissa measures the size of fractions A_0 to A_4 inclusive. The s. p. p. of fraction B could not be determined, because it was insoluble. It was extracted with boiling benzene for several days, but the solvent removed only 1.1 g. of rubber. This B fraction was a nearly white, fibrous mass with a nitrogen content of 9.4%.

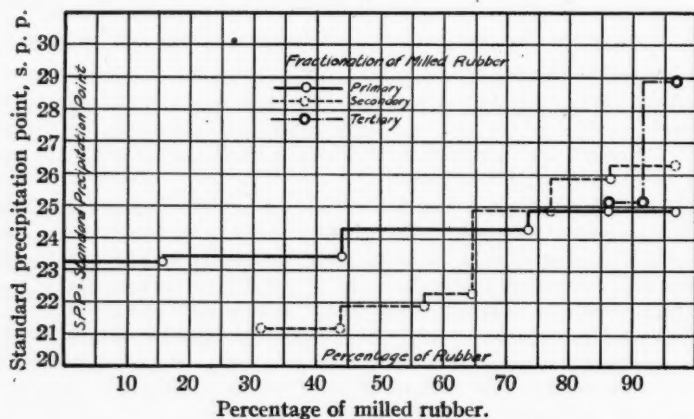


Fig. 1.—Fractionation of milled rubber.

Each of the primary cuts from A_1 to A_4 (viz., 81.2% of the rubber recovered) was refractionated. A_3 and A_4 were combined because they had the

TABLE II
SECONDARY FRACTIONATION OF FRACTIONS A_1 TO A_4 , viz., 81.2% OF THE RUBBER RECOVERED

Fractions	Amount, g.	S. p. p. in degrees	% based on 81.2% = 189.7 g.
A_1 { Top	28.6	21.2	12.2
Bottom	27.2	24.9	11.6
A_2 { Top	31.4	21.9	13.4
Bottom	24.5	25.9	10.5
A_3-4 { Top	17.9	22.3	7.7
Bottom	23.7	26.3	10.2
Total recovered	153.3		65.6
Remaining in solution	36.4		15.6
Total	189.7		81.2

same s. p. p. The refractionation was carried out at 50°; the results appear in Table II, and on the diagram.

The 36.4 g. of rubber remaining in solution could have been recovered in the manner used for A₀, in the primary fractionation; but this was considered superfluous for the present research.

The tables and diagram show that there is no indication of a single component, present in large proportion.

The fraction called "A₃₋₄ bottom," in Table II was then refractionated, to give the results shown in Table III.

TABLE III
TERTIARY FRACTIONATION OF A₃₋₄

Fractions	Amount, g.	S. p. p. in degrees	% based on 10.2% fractioned
A ₃₋₄ { Top	9.5	25.1	4.7
{ Bottom	11.3	28.9	5.5
Total	20.8		10.2

The efficiency of the separation method is illustrated as follows: A 10-g. specimen (s. p. p. 35°) obtained from *unmilled* rubber and a 10-g. sample (s. p. p. 28.9°) obtained from the fraction called [A₃₋₄, bottom], in Table III, were dissolved in the same batch of benzene, and separated by fractional precipitation. A single fractionation yielded 11.5 g. of s. p. p. 34.9° and 85. g. of s. p. p. 28.5°. This experiment demonstrates that the fractionation method separates with ease individual components.

The appearance of the various cuts was as follows. The fractions with low s. p. p. were almost colorless, transparent and very tacky. The higher s. p. p. fractions were less tacky, and they were yellow; in spite of the color, they did not have the appearance of oxidized rubber.

Conclusion.—Fractional precipitation shows that *milled* rubber is constituted of a continuous series of undefined components. Milling degrades the components of *unmilled* rubber into materials of lower s. p. p. without producing a single predominating component.

Summary

The composition of *milled* rubber has been investigated by a method based on fractional precipitation from a benzene-alcohol mixture. This has shown that milled rubber is made of a continuous series of undefined components, without a single predominating individual. The same method had previously shown that one single individual constituted more than one-half of unmilled rubber.

COLUMBUS, OHIO

Studies of Polymers and Polymerization

IV. Observations on the Polymerization of Isoprene and 2,3-Dimethylbutadiene-1,3

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Abstract

The polymerization of isoprene and dimethylbutadiene at temperatures ranging from 10° to 145° C. has been studied with reference to the nature of the dimeric products and the influence of the temperature and period of heating on the extent of polymerization, the ratio of oil to rubber and the molecular weight of the rubber and viscosity of its sols. There was no evidence of the formation from either diene of an open-chain dimer, polymerizable to rubber, such as the " β -myrcene" of Ostromislenski. The ratio of oil:rubber from a given diene is approximately constant in different periods of polymerization at a given temperature. The ratio increases with rise of temperature. Isoprene gives far more oily by-product than does dimethylbutadiene. As polymerization progresses, the molecular weight of the rubber and the viscosity of its sols rises. The higher the temperature of polymerization, the lower is the molecular weight ultimately attained. The polymerization is catalyzed by air. The viscosity of the sols of the synthetic rubbers is low and falls on keeping, owing to oxidation.

Ostromislenski^{27,28} has described the preparation from isoprene, by heating, of a dimer, " β -myrcene," for which he suggested the constitution $\text{CH}_2\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{CMe}\cdot\text{CH}\cdot\text{CH}_2$, and which, he stated, is polymerizable to rubber. If these observations can be substantiated, they are clearly of first-rate significance in regard to the mechanism of the polymerization of isoprene to rubber, and in regard to the constitution of the latter, and the establishment of the constitution of " β -myrcene" is a matter of importance. The present work was undertaken first with the object of isolating and studying " β -myrcene" or other simple intermediate products in the polymerization of isoprene to rubber. All attempts to isolate " β -myrcene" were, however, unsuccessful. The procedures described by Ostromislenski were carefully followed, but no evidence of the formation of the substance was obtained (*vide infra*). The only oily products, described later, which could be isolated when isoprene and dimethylbutadiene were polymerized by heat were cyclic dimers such as have been described by previous authors. These compounds are not further polymerizable to rubbers; they are not intermediate steps in the passage from the dienes to rubbers, and have no special significance in regard to the mechanism of the polymeric process by which rubbers are formed.

Following the examination of the oily polymers, experiments were carried out on the influence of temperature and time of heating on the polymerization of isoprene and 2,3-dimethylbutadiene-1,3, with special reference to the yields of oily and rubber-like polymers, respectively, and with reference to the molecular weight of the rubber and the viscosity of its sols. The most important data are summarized in Table I.

The results at 145° C. are in good accord with those obtained by Lebedev^{20, p. 1313} at 150° C. At this temperature he found the total polymerizate from isoprene to be 53 per cent after 5 hours and 79 per cent after 15 hours, while from dimethylbutadiene the total polymerizate after 15.5 hours was 39.7 per cent. He

found that when the polymerization of isoprene at 150° C. was complete, the product contained only 10 per cent of rubber.

As an examination of Table I shows, the rate of polymerization of isoprene when heated is greater than that of dimethylbutadiene. This is perhaps somewhat unexpected, as the authors have observed, in accord with most previous workers, that at room temperature dimethylbutadiene undergoes polymerization far more readily than isoprene. Samples of the former were generally observed to undergo complete polymerization to typical, white, cauliflower masses when kept for a year or two. Kondakov,¹² who first observed the spontaneous polymerization of dimethylbutadiene, found it to be complete in 1 year, whereas a sample of isoprene kept for 4½ years showed no separation of solid polymer and only about 16 per cent polymerization to rubber. Even when considerably diluted, samples of dimethylbutadiene were observed by Macallum and Whitby²³ to undergo, on keeping, conversion to the solid polymer after 2 or 3 years. Thus, *e. g.*, a fraction prepared from pinacone, boiling at 90° to 100° C. and containing a large proportion of pinacoline, showed on keeping considerable separation of polymer.

TABLE I
POLYMERIZATION OF ISOPRENE AND 2,3-DIMETHYLBUTADIENE-1,3

Time (Hrs.)	Isoprene				2,3-Dimethylbutadiene-1,3			
	Oil, %	Rubber, %	Mol. Wt.	Rel. Visc. ^a	Oil, %	Rubber, %	Mol. Wt.	Rel. Visc. ^a
<i>At 85° C.</i>								
97.5	9.07	17.05	4589	4.62				
101	7.9	16.25			0.9	10.5	2318	3.69
154					1.5	13.8	3345	3.83
250					2.7	19.6	3524	4.55
900		35.3	5715	8.20		49.7	3483	9.21
<i>At 145° C.</i>								
5.25	38.2	10.03	3291	3.14				
12.5	54.7	15.56	3936	4.69	11.1	15.6	2138	2.3
<i>At 45° C.</i>								
2628					Trace	19.25	2106	2.76
<i>At 10° C.</i>								
1 year	0.005	0.01		6.13 ^b				
<i>At room temp.</i>								
80 days					None	3.45	1926	1.99
4½ years	1.0	16.6	2312	13.4 ^c				

^a Relative viscosity at 30.1° C. of sol containing approx. 0.68 g. per 20 cc. benzene.

^b Relative viscosity at 30.1° C. of sol containing approx. 0.492 g. per 20 cc. benzene.

^c First fraction (see page 557).

Heat polymerization leads to the formation of a much larger proportion of oily by-products in the case of isoprene than in that of dimethylbutadiene. Increase in the temperature applied raises the proportion of oil to rubber in both cases. In the experiments at 145° C. the oil formed from isoprene is more than three times the amount of rubber formed. This makes it clear that the temperatures specified for the polymerization of isoprene to rubber in certain patents (*e. g.*, ⁴) are too high.

Some uncertainty attaches to the figures given for the molecular weight of the polymeric products, owing to the fact that the results of cryoscopic determinations were affected by the concentration of the solutions used. The results may, however, be considered as approximately correct, and, regarded broadly, show that on heating either of the dienes at a given temperature the molecular weight of the rubber produced increases as the percentage of the diene which has

undergone polymerization rises. Further, the higher the temperature applied to produce polymerization, the lower is the molecular magnitude of the rubber produced after similar amounts have been formed. And again as polymerization at a given temperature progresses, the viscosity of sols of the product rises. These generalizations are all in accord with those established by Whitby and Katz^{37,38} in a study of the polymerization of indene, namely, that, as polymerization by heat progresses at a given temperature, the state of polymerization rises, and the higher the temperature applied, the lower is the state of polymerization which is attainable in the ultimate product.

Since the polymerization of dimethylbutadiene at 85° C. is accompanied by the formation of only small quantities of oily, dimeric by-products, it was possible to follow the course of the polymerization by following the change of the refractive index. The results obtained in this connection are illustrated by the curve in Fig. 1. The refractive index changed rapidly at first, and then the rate of change

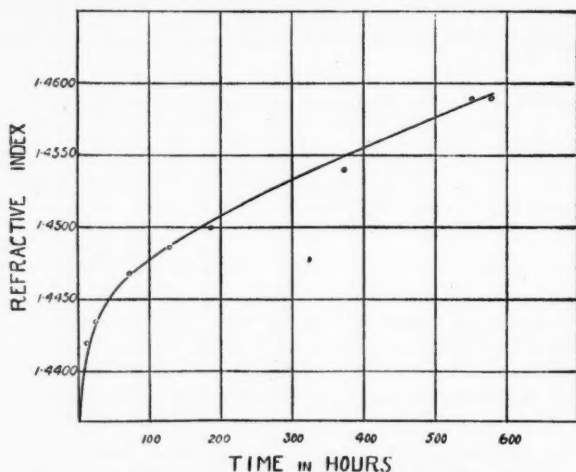


Figure 1—Change of Refractive Index of Dimethylbutadiene with Heating at 85° C.

slowed up considerably. This is in accord with the prior experiments (the results of which are given in Table I), in which the polymerization products were isolated and weighed; polymerization proceeds rapidly up to a certain point and then slows down. During the first 24 hours' heating at 85° C. the refractive index of dimethylbutadiene rose from 1.4367 to 1.4435, whereas after heating for 15 days and 12 hours, it rose only to 1.4540.

The rubber obtained by the polymerization of dimethylbutadiene at 85° C. dispersed in a few hours when placed in benzene, whereas that obtained by its polymerization at room temperature, which is presumably of much higher molecular weight, only swelled in benzene, and had not dispersed after two months' standing.

By fractional precipitation it was found possible to separate dimethylbutadiene rubber into fractions which gave sols possessing at the same concentration different viscosities. This shows that the polymeric products consist of a mixture of polymers representing different degrees of polymerization. A similar heterogeneity has previously been shown in the case of polymerizates from indene,^{37,38} vinyl acetate,⁴⁰ and styrene.^{31,39}

Measurements made of the iodine absorption of dimethylbutadiene rubber point to the presence, as in natural rubber, of one double bond for each unit of the diene which has gone to form the polymer. This is in agreement with the molecular refraction as determined by Macallum and Whitby.²²

Sols of the rubbers obtained by the heat polymerization of both isoprene and dimethylbutadiene were observed to suffer a marked decrease in viscosity on keeping. For instance, the time of flow of a sol of dimethylbutadiene rubber which was originally 155.4 seconds had fallen after only 25 days in the dark to 81.6 seconds, and that of a sol of isoprene rubber from a time of flow of 221.2 seconds, 7 days after its preparation to 125.2 seconds after 46 days. That the fall in viscosity is due to the gradual oxidation of the synthetic rubber is made apparent by the further observation that the addition of an antioxidant, dimethylaniline, prevented a fall in the viscosity on keeping. Figure 2 shows the fall in viscosity

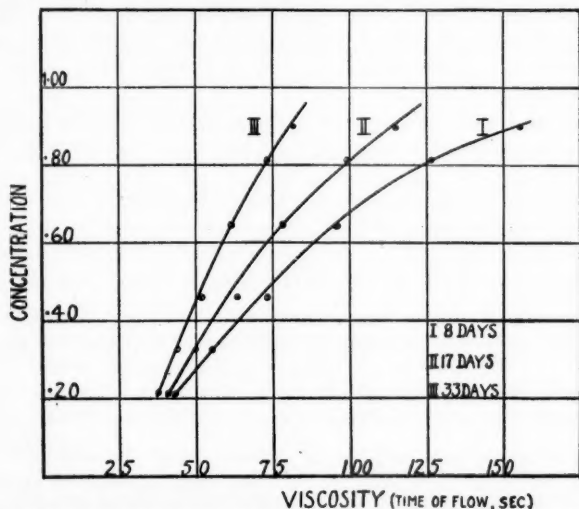


Figure 2—Fall in Viscosity of Sols of Dimethylbutadiene Rubber on Keeping. Time of Flow Measured after Keeping Sols for 8, 17, and 33 Days

of sols of methyl rubber with time. The fall resulted from a permanent change in the rubber, since on recovering the polymer from a sol which had been kept it was found to have been converted into a sticky product different from the originally tough, elastic rubber.

Various inorganic halides were found to bring about the rapid catalytic polymerization of isoprene and dimethylbutadiene in the cold. The most vigorous catalyst observed appeared to be antimony pentachloride. Other powerful catalysts were stannic chloride, antimony trichloride, and aluminum chloride. Less effective were ferric chloride and bromide, thorium bromide, boron trichloride and tribromide, and dichloroacetic acid. These yielded a small quantity of polymer after standing 2 days. The polymers produced by the various halides were in all cases white or pale-colored substances, inelastic and quite unlike rubber. Apparently they are isomers of rubber. It is interesting to note that the halides converted natural rubber into similar products. On adding them to a solution of rubber in benzene highly colored complex products were formed first, and these, when alcohol was added, yielded white or pale yellow powders, mostly soluble

in benzene to only a slight extent. A similar observation in the case of the action of stannic chloride on rubber has been made by Bruson, Sebrell, and Calvert.⁶

Dimers

By heating isoprene at 280–290° C. for six hours, G. Bouchardat⁵ obtained among other products a terpenic fraction which boiled chiefly at 176–181° C., and had d_4^{20} 0.866, d_4^{21} 0.853. It was designated terpilene. Tilden³² heated isoprene at 250–280° C. for 12 hours, and found on distillation that about one-half of the material came over between 170° and 180° C. Wallach³⁴ identified dipentene in oils such as those just mentioned. He heated isoprene for some hours at 250–270° C. and obtained, together with high boiling polymerization products, a hydrocarbon, boiling at 180° C., which yielded a tetrabromide identical with dipentene tetrabromide. Wallach³⁴ also identified dipentene in the oil obtained by the destructive distillation of rubber, and it came to be generally considered that dipentene constitutes the major part of the terpene fraction in the oil obtained by the dry distillation of rubber. Harries,⁸ however, states that dipentene constitutes at most one-third of the "dipentene fraction" boiling at 150–200° C. obtained from rubber.

Harries further states that on heating isoprene at 300° C. he found only a little dipentene to be formed, the main product being another terpene boiling at 64–66° C. (12 mm.).

Lebedev^{18,19,21} subjected isoprene to a lower temperature than the temperatures mentioned above, namely, 150° C. He obtained besides dipentene another dimer which he considered to be 1,3-dimethyl-3-ethenyl-6-cyclohexene. The properties of the two fractions he obtained were as shown in Table II.

TABLE II

PROPERTIES OF FRACTIONS OBTAINED BY LEBEDEV ON HEATING ISOPRENE TO 150° C.

Fraction	B. p. at 760 Mm.	B. p. at 9 Mm.	d_4^{20}	n_D^{20}
No. 1 (Lebedev's dimer)	160–161° C.	44° C.	0.8331	1.46581
No. 2 (Dipentene)	174–175° C.	58° C.	0.8454	1.47428

In the experiments recorded in the present paper Lebedev's dimer was not encountered. Harries⁹ in a later paper than that mentioned above reports on the terpene fraction of freshly polymerized isoprene, without, however, specifying exactly the conditions under which polymerization was carried out, although apparently they involved heating isoprene with acetic acid at a temperature of about 100° C. The main quantity he found to boil at 63–65° C. (14 mm.) and to show d_4^{18} 0.8451, n_D^{18} 1.4708. It gave only a little dipentene tetrabromide. Harries considered that it probably consisted for the greater part of an open-chain dimer of isoprene of the same formula as that later assigned to "β-myrcene" by Ostromislenski (*infra*). The product was not investigated further. Aschan also has reported on a dimeric product from isoprene, which he regards as quite distinct from dipentene, but which he classifies as a cyclic compound of the sylvestrene series, and to which he assigns the name diprene. After being allowed to stand at ordinary temperature for 10 years, he found that 250 g. of isoprene yielded² 7 g. of dimeric material, the major fraction of which had the properties recorded below and yielded a dihydrochloride which melted at 51.5–52° C. and depressed the melting point of dipentene dihydrochloride when mixed with the latter (m. p. of dipentene hydrochloride: 48–50° C.). Aschan^{1,3} also examined somewhat larger quantities of dimeric material obtained by the polymerization of isoprene "at temperatures below 100° C." (it is not stated whether a catalyst was used in the polymerization), and concluded that this too consisted mainly of diprene.

The physical properties of the main fraction obtained by distillation under ordinary and under reduced pressure are shown below (b and c). A sample of "diprene" isolated in the present investigation from isoprene which had been allowed to stand at room temperature for $4\frac{1}{2}$ years was proved to contain dipentene by the preparation from it of dipentene tetrabromide.

TABLE III
PROPERTIES OF ASCHAN'S DIPRENE

Polymerization Conditions	Boiling Point, ° C.	d_4^{20}	n_D
(a) By cold polymerization of isoprene	171-172 (769 mm.)	0.8535	
(b) By polymerization of isoprene below 100°	171.5-173 (752 mm.)	0.8481	1.46960 ^a (23.4° C.)
(c) By polymerization of isoprene below 100°	68.5-69 (16 mm.)	0.8476	1.46946 (23.2° C.)

^a The figure given in the reference, *viz.*, 1.49660, is apparently due to a clerical error.

With the possible exception of the dimeric products mentioned by Harries⁹ all the dimers just described as being obtained from isoprene are clearly cyclic compounds. The observed refractive index for both Lebedev's and Aschan's products agrees reasonably well with the calculated value for $C_{10}H_{18}$ $\left[\frac{2}{3} \right]$. An entirely different dimer, *viz.*, " β -myrcene," has, however, been described by Ostromislenski.^{27,28} It is stated that this hydrocarbon is formed when isoprene, either alone or in the presence of a catalyst, is allowed to stand at ordinary temperature or is heated to not above 150° C.²⁷ It is stated to be the chief product when isoprene is heated to 80-90° C. for 3-5 days.²⁸ It is also stated to be an open-chain compound containing three double bonds of which two form a conjugated system; to be polymerizable quantitatively to rubber; to yield, like other conjugated hydrocarbons, an amorphous solid with an aqueous solution of sulfur dioxide. It is distinguished from the dimers of isoprene described by all other authors in possessing a much higher refractive index than they. The present authors find, it may be mentioned here, that the value recorded by Ostromislenski is too high even for the assumed constitution.

" β -myrcene"

B. p. 63.5° C. (20 mm.), n_D^{26} 1.53681, d_4^{20} 0.8472. MR_D : Found, 50.01; calcd., 47.8 (for $C_{10}H_{18}$ $\left[\frac{2}{3} \right]$ + 0.98 for exaltation).

As early as 1900-1902 Kondakov¹⁴ had suggested "that a transient stage in the polymerization of these hydrocarbon conjugated dienes consists of dimeric, open-chain isoprenes, containing several double bonds in the molecule." But prior to Ostromislenski's work on β -myrcene there was no clear record of the isolation of such an open-chain dimer. In the present investigation attention was particularly directed to β -myrcene when studying the oily dimers from isoprene. The conditions under which the polymerization of isoprene were brought about were all conditions which Ostromislenski has indicated as suitable for the preparation of β -myrcene, but in no case was any evidence found of the presence of this material, which should be so easily recognizable on account of its high refractive index. None of the products underwent polymerization when treated with sodium and barium peroxide as directed by Ostromislenski, and none reacted with sulfur dioxide solution except apparently in so far as some of the fractions were contaminated with isoprene. The iodine absorption of one of the products was determined and found to correspond to the presence of two double bonds only. Further, the oil obtained in one experiment was subjected to bromination and proved to contain a considerable proportion of dipentene.

The temperatures at which isoprene was polymerized were (a) room temperature, (b) 85–92° C., (c) 145° C. Polymerization was also carried out at 90° C. in the presence of benzoyl peroxide. The physical properties of the main fractions are shown in Table IV.

TABLE IV
DIMERIC FRACTIONS FROM ISOPRENE

Polymerization Conditions	Boiling Point, ° C.	n_D	d_4^{25}
Expt. A. 5 days at 92° C.			
Fraction 2	172–174 (760 mm.)	1.4750 (16.5° C.)	
Fraction 3	174–176 (750 mm.)	1.4753 (16.5° C.)	
Expt. B. 98 hr. at 85° C.			
Fraction 3	171–174 (760 mm.)	1.4705 to 1.4710 (26° C.)	
Fraction 4	174–175 (760 mm.)	1.4723 to 1.4726 (26° C.)	
Expt. E. 10 days at 90° C. with 5% benzoyl peroxide			
Fraction 1	60–61.5 (10.5–11 mm.)	1.4710 to 1.4713 (25° C.)	0.8320
Fraction 2	61.5 (10.5–11 mm.)	1.4727	0.8380
Expt. F. 4½ years at room temperature		1.47120 (23.4° C.)	

A definitive investigation of the dimeric polymerizate from isoprene probably demands the careful fractionation and study of a much larger quantity of material than has been employed by any workers hitherto. In the opinion of the present authors the material is preponderantly dipentene. The fact that on bromination it yields a considerable quantity of oily bromide in addition to solid dipentene tetrabromide can be explained by the presence of a relatively small quantity of material other than dipentene, as the bromination of even a stock sample of redistilled dipentene from another source gave a fair quantity of oil along with the solid. The formation of dipentene from isoprene over a wide temperature range has now been established. Wallach³⁴ shows that it is formed at 250–270° C.; Lebedev^{18–21} that it is formed at 150° C.; and the present authors that it is formed at 92° C. and at room temperature. Another point to be noted is that, in the isolation of the dimeric polymerizate of isoprene, even after the apparently thorough removal of unchanged isoprene by distillation on the water bath at ordinary pressure, the dimeric material was observed to be contaminated with isoprene (see Expt. B, p. 556). The presence of such contamination in the products of earlier investigators may possibly account for some of the deviations in physical properties recorded for the products.

As in the case of isoprene, an examination of the dimeric polymerizate from dimethylbutadiene failed to indicate the presence of an open-chain compound, the products obtained being cyclic ones similar to those described by previous workers.

Experimental

Preparation and Purification of Isoprene.—Crude isoprene was prepared from dipentene* by means of a modified "isoprene lamp."† The essential features of the apparatus are shown in Figs. 3 and 4. In Fig. 3, A is a three-liter Pyrex flask containing the heating element B which serves to crack the dipentene vapor. C is a condenser (with inner tube of Pyrex glass) through which water at 45–50° C. is circulated. D is a spiral condenser (with more coils than shown in the diagram) through the jacket of which cold water is circulated. E is a 300-cc. flask cooled

* Kindly supplied by the Hercules Powder Company.

† Cf. Reference No. 10.

to -10°C . by means of an ice-salt mixture in the bath F. G is placed in a Dewar flask, H, filled with ether cooled by solid carbon dioxide. It serves to collect any isoprene which escapes from E.

Figure 4 shows diagrammatically the heating element, B, the upper diagram being a plan. The element consisted of six feet of No. 28 gage platinum wire, F, threaded through holes in two perforated discs of asbestos slate, B, 4.75 in. apart, and forming eleven vertical strands. The holes in the plates for the passage of the wire were made as large as the strength of the plates would permit, in order to allow of the free passage of vapors. The plates, 0.125 in. in thickness and 1.5 in. in diameter, were attached to a copper wire, C, 0.125 in. in diameter, by means of nuts soldered to the rod on either surface of each plate. This rod acted as one terminal. The other terminal, E, was attached to the end of the platinum wire

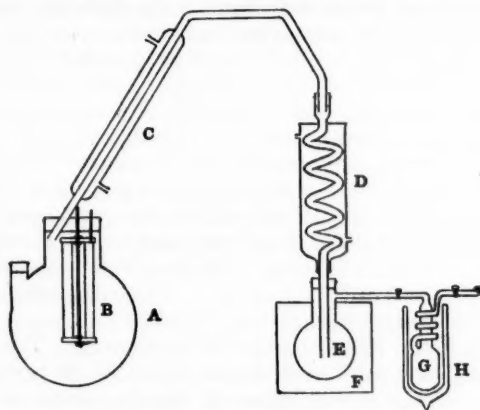


Figure 3—Modified "Isoprene Lamp"

which had been brought over the edge of the upper plate. It may be mentioned that a nichrome element could not be used in place of platinum, as after a few minutes' running it became heavily coated with carbon.

In addition to the cracking apparatus just described, an apparatus for cracking under reduced pressure was built on lines similar to those described by Staudinger and Muntwyler.²⁵ It was, however, found to be considerably more inconvenient and troublesome than the former apparatus.

In operating the "lamp" described, the charge of dipentene was 450 cc. only, as with this charge the apparatus worked most efficiently. After the charge had been brought to the boiling point and the air displaced, the heating coil was brought to, and maintained at, a dull red heat by 7.5 to 8.5 amp., 110 volts d. c., while the dipentene was kept boiling fairly rapidly. Owing to the gradual deposition of carbon on the platinum, the efficiency fell as the run proceeded. Hence each morning before starting a run the platinum was cleaned by heating the coil to a bright red heat. Further, as a run proceeded accumulation of resins in the liquid left in the cracking flask led to a falling-off in the rate of isoprene formation. Hence before each run the flask was cleaned out. In a typical run a charge of 450 cc. of dipentene gave in 7 hours a distillate of 270 cc. and left a residue of 160 cc. The distillate gave on redistillation 190 cc. of an isoprene fraction (b. p. 27.5° to 37°C .), the balance being unchanged dipentene.

Four liters of crude isoprene prepared by the lamp were dried over calcium chloride and fractionated several times. The method of purification at first em-

ployed was one described by Ostromislenski.²⁶ Isoprene (1500 cc.) boiling at 33–36° C. was allowed to stand at room temperature over 16 g. of sodium wire and 135 g. of barium peroxide for at least two days; it was then refluxed for one hour and fractionated. This gave 1300 cc. of isoprene boiling at 33–35° C. As it appeared in the first experiment (Experiment A) on polymerization, that the above method does not yield isoprene of very high purity, the material used in all but the first experiment was subjected to further purification involving conversion to the tetrabromide.*

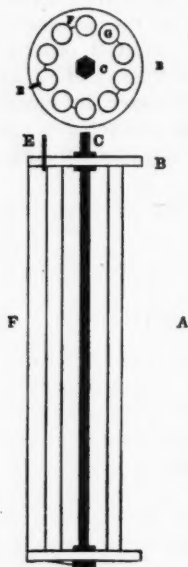


Figure 4—Cracking Element for Isoprene Lamp

Following the procedure of Gustavson⁷ 100 cc. of isoprene, dissolved in 100 cc. of chloroform, were introduced into a two-liter flask fitted with a reflux condenser, dropping funnel, and mechanical stirrer. The flask was cooled in a bath to –10° C. and a previously cooled solution of 320 g. of bromine in 500 cc. of chloroform was added drop by drop. It was found after five or six experiments that these concentrations were the most convenient. In more concentrated solutions a certain quantity of hydrobromic acid was evolved. The solution of bromides thus obtained was washed with aqueous soda solution until colorless and the chloroform layer was dried over anhydrous potassium carbonate. The chloroform was distilled off and the concentrate, generally brown in color, distilled *in vacuo*. The three main fractions were as follows: I, 60–70° C. at 12 mm. This, containing amylene bromides, was discarded. II, 88–94° C. Isoprene dibromide. III, 155–160° C. Isoprene tetrabromide. The yield of the second and third fractions was about 75–80 per cent. After three or four distillations *in vacuo*, colorless, or almost colorless, products were obtained. As they turned dark on standing, they were used at once. Only a small proportion of the dibromide was obtained.

The regeneration of the isoprene from the tetrabromide was carried out as follows: 320 g. of isoprene tetrabromide were added slowly by means of a dropping funnel to 450–500 cc. of alcohol in which were suspended 262 g. of zinc dust, the latter being added in three portions, and the reaction mixture being kept in constant agitation by an electrically driven stirrer through one neck of the flask (three-necked type). To this flask was attached a reflux condenser kept at a temperature of 45–50° C. The rest of the apparatus for collecting the isoprene was similar to that in Fig. 3. Traces of alcohol carried over with the isoprene were removed by washing. The yields by this method were 85 to 90 per cent of the theoretical. If stirring was not applied, they were much poorer. The same procedure was applied for the regeneration of the isoprene from the dibromide fraction, the yields being 75–85 per cent.

Finally the regenerated isoprene was dried over calcium chloride and distilled. The distillate was then allowed to stand for several days over sodium wire and redistilled. The boiling point of the pure product was 33.4° to 33.9° C. at 744 mm.

Preparation of 2,3-Dimethylbutadiene-1,3.—Pinacone hydrate was prepared from carefully dried and redistilled acetone by reduction with amalgamated aluminum as follows. To 200 g. of 20-mesh aluminum in a perfectly dry three-liter flask a solution of 30 g. of mercuric chloride in 300 cc. of acetone was added rapidly with agitation. The mixture was left undisturbed for 15–20 min., and then 10 g. of

* Cf. References 15 and 24.

finely divided zinc chloride and 100 cc. of acetone was added. The mixture was allowed to stand $1\frac{1}{2}$ –2 hrs., with frequent vigorous agitation, to prevent caking of the aluminum. Then 500 cc. acetone and a solution of 30 g. of mercuric chloride in 600 cc. of acetone were added dropwise over a period of four hours at such a rate as to keep the liquid boiling, 100 cc. of one and 100 cc. of the other reagent being added alternately. The flask, covered with a cloth, was allowed to stand overnight. Generally it was found refluxing slowly in the morning. In all the reaction took 35–40 hrs. Moisture was excluded. Stirring was not found to be necessary so long as the aluminum was kept in a loose condition. Finally the flask was heated on the water bath for two hours. Then 1200 cc. of water were added gradually to decompose the complex, the mixture was boiled for two hours, allowed to cool to 40° C., and filtered. The mass was extracted with four 1000-cc. portions of acetone. The filtrate and washings were concentrated to about 2000 cc. and the supernatant oil removed. The aqueous liquid on standing overnight in an ice box deposited crystals of pinacone hydrate. The oil, which consisted of mesityl oxide, phorone, etc., deposited crystals of pinacone. The total yield of pinacone hydrate was about 350 grams. The product was recrystallized twice by dissolving it in an equal weight of hot water, filtering, and cooling in ice. Water of crystallization was removed from the pinacone hydrate by distillation, practically all the water being given up under 135° C. Pinacone carried over to the extent of 10–15 per cent was recovered. A long air condenser and well-cooled receiver were used. Yield: 85–90 per cent. The use of potassium hydroxide and potassium carbonate as dehydrating agents was not as convenient as the method described.

For conversion of pinacone into the diene the following gave the best yields of the methods tried: pinacone (500 g.) was distilled with 2 g. of 48 per cent hydrobromic acid,¹⁶ half of the pinacone being added through a separating funnel. The reaction proceeded very slowly, but after 24 hrs. most of the pinacone had reacted. The hydrocarbon layer of the distillate gave after one fractionation 55 per cent of the theoretical yield of dimethylbutadiene boiling from 68° to 72° C. By repeated fractionation of the higher boiling fractions a further quantity of diene was recovered, the total yield from 3000 g. of anhydrous pinacone being 1600 g. of dimethylbutadiene (75 per cent).

Conversion of pinacone to the diene by means of potash alum, by means of sulfanilic acid—methods used by Macallum and Whitby²³—or by means of potassium bisulfate did not give as good yields as the procedure just described.

Impurities in the diene, mainly pinacoline, were removed by treating the carefully dried and fractionated product with sodium. After several such treatments, the final product had—b. p. 69.5–70.5° C.; n_D^{22} 1.4370 (one sample), n_D^{24} 1.4367 (another sample). Kondakov gives n_D^{20} 1.4375, and Macallum and Whitby,²³ n_D^{20} 1.4376.

Polymerization of Isoprene

Examination of the Oily By-Products.—*Experiment A.* Following a procedure of Ostromislenski²⁸ for the preparation of “ β -myrcene,” 200 g. of isoprene were heated in an autoclave for five days at a temperature ranging from 85° to 95° C., but for the most part at 92° C. Unchanged isoprene (56 per cent of the total) was removed from the resulting colorless, syrupy liquid by distillation from a water bath. The residue was then distilled with steam and gave 65 cc. (27 per cent of the isoprene used) of a clear, colorless oil and 30 g. (15 per cent) of a rubber-like residue.

The oil, which had a peculiar odor unlike that of a stock sample of dipentene,

was dried in ether over anhydrous sodium sulfate, and then distilled under 10.5 mm. It distilled over between 53.5° and 56.5° C., leaving a small residue of very viscous, colored oil. The residue when treated with alcohol gave a fine crystalline precipitate, the nature of which was not investigated.

Examination of the distillate gave the following results: mol. wt. (cryoscopically, in benzene), 139.9 (calcd. for $C_{10}H_{16}$: 136.2); $n_D^{14.5}$ 1.4769. (A sample of dipentene gave $n_D^{14.5}$ 1.4765.) It gave only a trace of amorphous, white precipitate when treated, even for several days, with a concentrated aqueous solution of sulfur dioxide. When heated according to Ostromislenski's instructions²⁸ with sodium and barium peroxide in a glass tube for three days at 100° C., it gave no evidence of the occurrence of polymerization.

TABLE V IODINE ABSORPTION, BY HANUS SOLUTION, OF OIL OBTAINED IN EXPERIMENT A				
Period of absorption (hrs.)	5	5.5	7.5	24
No. of double bonds	1.8	1.8	1.9	2.1

Distillation under atmospheric pressure yielded the following fractions. There was no sign of polymerization during this distillation.

Fraction 1, up to 172° C. (corr.). Fraction 2, 172–174° C.; $n_D/16.5^\circ C.$, 1.4750. Fraction 3, 174–176° C.; $n_D/16.5^\circ C.$, 1.4750. Fraction 4, 176° C.–end.

Fractions 2 and 3, which comprised most of the oil, were shown by bromination to contain a considerable proportion of dipentene. On distilling a sample of dipentene most of it came over between 174° and 176° C. (b. p. of pure dipentene is given as 175–176° C.). As Fraction 2 above was equal in volume to Fraction 3, it appears that the oil from isoprene contains one or more other cyclic dimers in addition to dipentene. The bromination results are also in agreement with this assumption.

Samples of Fractions 2 and 3 and also of dipentene were diluted with four parts of absolute alcohol and four parts of absolute ether and saturated in the cold with bromine. They were allowed to stand in an ice box for two weeks, and the solutions were then evaporated. The residue consisted in each case of crystals mixed with a very viscid oil, but from dipentene the crystals formed a greater proportion of the whole than from the fractions of the other oil. After several recrystallizations from ether each of the batches of crystals melted at 125° C.

Experiment B. Since the isoprene used in Experiment A had been purified only by means of sodium and barium peroxide, and since an iron autoclave had been used, the experiment was repeated using sealed glass test tubes and highly purified isoprene (from the tetrabromide). Pure isoprene (300 cc.) was heated in six sealed glass tubes at 85° C. for 98 hrs., all the details given by Ostromislenski in one place* for the preparation of β -myrcene thus being very exactly duplicated. Unchanged isoprene was removed by distillation at atmospheric pressure and the oil was then separated from the rubber-like high polymer by distilling, until no further loss in weight occurred, at a pressure of 9 mm. which was later reduced to 1 to 2 mm. The distillate was collected in a flask cooled in solid carbon dioxide and ether. The oil, amounting to 19.5 g., was dried over calcium chloride and again distilled under a pressure of 7 mm. Only a very slight residue remained. Refractionation of the oil gave the following results at 7 mm. Hg. Fraction 1: 7.3 g.; b. p. up to 53° (7 mm.), mostly at 52–53° C.; n_D^{25} 1.4540. Fraction 2: 11.4 g.; b. p. 53–54° C. (7 mm.); n_D^{25} 1.4713. Fraction 3: 0.75 g., residue. The low refractive index of Fraction 1 was shown to be due to the presence of some isoprene.

* Cf. Reference 30, p. 94.

These fractions were then distilled at atmospheric pressure with the results shown in Table VI.

TABLE VI
PROPERTIES OF FRACTIONS OBTAINED FROM EXPERIMENT B

Fraction	Boiling Point, ° C.	Refractive Index at 26° C.	Behavior with an Aqueous Solution of SO ₂
1. Isoprene present	Up to 128		Gave a heavy, white precipitate
2.	128-171 (mainly 169-171°)	1.4667 to 1.4670	Slight precipitate
3.	171-174	1.4705 to 1.4710	Very slight precipitate
4.	174-175	1.4723 to 1.4726	No precipitate
5. Residue (slightly brown viscid oil)		1.4827 to 1.4820	

The residue was distilled under reduced pressure and a few drops of a clear, colorless oil were obtained; n_D^{25} 1.4730.

None of the fractions obtained (discarding No. 1) showed any tendency to polymerize when treated with sodium and barium peroxide for three days at 100° C.

Clearly the oil obtained in this experiment was substantially the same as that obtained in Experiment A.

Experiments C and D. In these experiments a higher temperature was applied, isoprene being heated for 5.25 and 12.5 hrs., respectively, at 145° C. The oil proved to be essentially similar to that obtained in the two preceding experiments, as was shown by the boiling point and refractive index of the fractions into which it was separated.

Experiment E. In a second procedure given by Ostromislenski for the preparation of β -myrcene²⁷ pure isoprene is heated with 5 per cent of benzoyl peroxide for 10 days at 90° C. Using the same procedure, 50 cc. of pure isoprene and 1.7 g. of benzoyl peroxide were introduced into each of three Pyrex tubes, sealed, and heated as mentioned above. As in previous experiments, most of the isoprene remained unchanged; after its removal the residue was steam-distilled, the oil separated, dried over calcium chloride, and distilled under reduced pressure. At 10.5 mm. of mercury the boiling point rose rapidly to 61.5° C. and remained there until the close of the distillation. Two fractions were obtained. Fraction 1: b. p. up to 61.5° C. (mostly at 60-61.5°) at 10.5-11 mm.; n_D^{25} 1.4710 to 1.4713; d_4^{25} 0.832. Fraction 2: b. p. 61.5° at 10.5-11 mm.; n_D^{25} 1.4727; d_4^{25} 0.838.

The oil fractions behaved in a similar way to those obtained in preceding experiments.

No substance could be isolated in these experiments in any way comparable to the behavior of the so-called " β -myrcene."

Experiment F. About 50 cc. of isoprene were allowed to stand for 4½ years at room temperature in the dark in a bottle of 100-cc. capacity, the space above the liquid being filled with air. At the end of this period no separation of polymer had taken place, but the liquid, although not highly viscous, was noticeably more viscous than the original isoprene. The major portion was distilled at ordinary pressure from a water bath in order to remove unchanged isoprene; the dimeric oil was then removed by distillation at 17 mm., and the residue of crude rubber was weighed: 31.2 g. gave 0.31 g. oil (1 per cent) and 5.2 g. (16.6 per cent) rubber.

The oil, colorless, possessed a peculiar and somewhat ethereal odor; n_D 1.47125 at 23.2° C., 1.4710 at 23.6° C. It was brominated in solution in absolute alcohol and ether and the solution was allowed to stand in a refrigerator for 24 hours. The crystals which had separated were isolated and after five recrystallizations

from ether containing a little alcohol gave a colorless product melting at 123.5–124.5° C. A sample of dipentene tetrabromide prepared in the same way from redistilled dipentene melted at 124.5–125° C. A mixed melting point determination gave 123–124° C.

The crude rubber (5.2 g.) was dissolved in 40 cc. of benzene and poured dropwise into 200 cc. of absolute alcohol. A white rubbery clot formed. It was removed and dried in a vacuum until constant in weight (1.5875 g.). When dry it was clear, colorless, and elastic, but not strong. Data for the molecular weight of this fraction and for the viscosity of its sols are given in Table VII. The mother

TABLE VII
ISOPRENE RUBBER

Sample, Time and Temp. of Polymerization	Viscosity		Molecular Weight	
	Conc., G./20 Cc. Benzene	Relative Viscosity, Benzene = 1	Conc., G./20 Cc. Benzene	Mol. Wt.
(a) 97.5 hrs. at 85° C.	0.1290	1.54	0.2627	3348
	0.2025	1.81	0.6808	4870
	0.4710	3.10	0.6810	4893
	0.4997	3.24	0.6862	5158
	0.6810	4.62	0.8292	4680
	0.6862	4.66		(Mean: 4589)
	0.7285	4.79		
	0.8292	5.92		
	0.9316	6.44		
(b) 900 hrs. at 85° C.	0.1077	2.01		
	0.2946	3.92		
	0.6830	8.20	0.6830	5562
	0.7004	9.43	0.7004	5867
	0.8098	8.84 ^a		(Mean: 5715)
	0.9223	11.85		
(c) 5.25 hrs. at 145° C.	0.0715	1.14		
	0.2406	1.57	0.2406	2713
	0.5078	2.36		
	0.6681	3.09		
	0.6935	3.14	0.6935	3630
	0.7380	3.20	0.7380	3360
	0.9325	4.14	0.9325	3460
				(Mean: 3291)
(d) 12.5 hrs. at 145° C.	0.2317	1.97	0.2317	2613
	0.4440	3.03	0.4440	3617
	0.6947	4.65		
	0.6982	4.69	0.6982	4761
	0.8268	5.78	0.8268	4753
				(Mean: 3936)
(e) 1 year at 10° C. ±	0.0512	1.24		
	0.1172	1.60		
	0.2912	2.57		
	0.4920	6.13		
(f) 4½ years at room temp.	0.2907	5.0	0.4915	2308
	0.4915	7.9	0.6797	2315
	0.6797	13.4		(Mean: 2312)

^a Measurement after 10 days.

liquor from the above precipitate was evaporated to 25 cc. and a further quantity (75 cc.) of absolute alcohol was added. This precipitated a second fraction of rubber (2.3 g.), which, unlike the first fraction, was yellowish and somewhat sticky. Evaporation of the mother liquor gave a third fraction, also somewhat sticky and noticeably darker in color.

In addition to the isolation of rubber from the 4½-year old isoprene by distillation, rubber was isolated from a portion by precipitation. The old isoprene

(3.6578 g.), treated with 50 cc. of methyl alcohol, yielded a clot of colorless rubber weighing 0.2218 g. The mother liquor was then evaporated, the residue was taken up in 5 cc. benzene, and more precipitant was added. This gave a further quantity of 0.1496 g. rubber. The total rubber recovered was thus 10.2 per cent. The mother liquor contained a further fraction which presumably was in such a low state of polymerization that it was difficult to precipitate it.

Effect of Temperature and Time on the Polymerization of Isoprene.—After heating pure isoprene at the temperatures and for the periods specified, unchanged monomer was removed by distillation at ordinary pressure; then oily polymeric products were removed by distillation under reduced pressure until the distillation flask suffered no further loss in weight, and the yield of rubber was obtained by weighing the tared flask. The oil was collected in a receiver cooled with solid carbon dioxide and ether. The yield of oil was determined by evaporating the distillate under reduced pressure until no more diene came off. As the speed of polymerization is influenced by the volume of air in contact with the diene, a constant ratio of diene to air was employed in all but one of the experiments at 85° and 145° C. The tubes were of 165-cc. capacity and each contained 50 cc. of isoprene except in the experiment in which a heating period of 101 hrs. was applied. In the latter the tubes had a capacity of 90 cc. and contained 30 cc. of diene. The results are given in Table I.

Molecular Weight of Rubber Polymers and Viscosity of Their Sols.—The samples of synthetic rubber obtained in the above polymerization experiments were purified by dissolving them in pure anhydrous benzene and precipitating them with absolute alcohol, this procedure being repeated at least twice. After the greater part of the attached liquid had been expressed from the precipitated rubber, the latter was dried for 4–5 days in a desiccator evacuated by means of a Hyvac pump. All measurements were made immediately the samples were dry, as it was observed that even when they were kept in a vacuum of 9–10 mm. oxidation occurred rather rapidly.

Molecular weights were determined cryoscopically in benzene. In preparing the solutions, bottles containing the rubber and benzene were kept in the dark for four days with occasional shaking. Results obtained at different concentrations are shown in Table VII. Average values have been recorded in Table I.

A uniform procedure was followed in the preparation of sols of the samples for viscosity measurements, the samples being treated with 20 cc. of purified benzene in a 50-cc. bottle and kept for eight days in a dark cupboard, with shaking once a day. Measurements were made with an Ostwald viscosimeter at 30.1° \pm 0.02° C.

Cold, Catalytic Polymerization of Isoprene and Dimethylbutadiene.—To quantities of 0.5 cc. of isoprene a number of halides were added and the following observations made.

(a) *Stannic chloride* (2 drops). Polymerization complete in 3 hrs. yielding a clear, soft, amber colored, non-elastic mass, which when warmed showed elastic properties if squeezed, and which swelled but did not dissolve in benzene. Addition of alcohol converted it to a white powder.

(b) *Antimony pentachloride*. Two drops of undiluted reagent produced at ordinary temperature a violent reaction, forming a pitchy product soluble in benzene. At the temperature of solid carbon dioxide, the result was similar to that produced by stannic chloride at room temperature. Five drops of a 20% solution in chloroform had a similar effect, the product being orange colored.

(c) *Antimony trichloride*. The powdered reagent produced at room tem-

perature a violent reaction with charring; at the temperature of solid carbon dioxide, a result similar to that with stannic chloride.

(d) *Ferric chloride*. Only slight effect after 2 days.

(e) *Ferric bromide*. Gave a dark brown weak gel after 12 hours.

(f) *Aluminium chloride*. Complete polymerization after 24 hrs. to a yellow flaky mass only slightly soluble in benzene.

(g-i) *Thorium bromide*, 5 drops boron trichloride in 20 per cent chloroform solution, 5 drops boron tribromide in 20 per cent chloroform solution. Little or no evidence of polymerization after 24 hrs. in any of the three cases. Addition of alcohol after 48 hrs. precipitated a small amount of powdery polymer.

When a 3 per cent solution of rubber in benzene was treated with the following catalysts, viz., SbCl_3 , SnCl_4 , SbCl_5 , AlCl_3 , FeBr_3 , highly colored complexes were formed, which on the addition of alcohol yielded white or pale yellow powders, mostly only very slightly soluble.

Similar results to those obtained with isoprene were obtained by adding antimony pentachloride and stannic chloride to dimethylbutadiene.

Polymerization of Dimethylbutadiene

Examination of the Oily By-Products.—In no case did examination of the oily, dimeric polymerization products yield any evidence of the presence of an open-chain dimer analogous to " β -myrcene."

Pure dimethylbutadiene was heated at 85° C. for periods of 101, 120, 154, and 250 hrs., the quantity of diene taken being 100 cc. in all cases except the second, where it was 375 cc. Unchanged diene was removed by distillation under ordinary pressure and the oily polymerization products were then isolated by distillation under reduced pressure. The yield of oil from a single experiment was so small that the oil from the four experiments (5-6 cc.) was combined and subjected to examination. It boiled at 80° C. (10 mm.) and showed n_D^{26} 1.4775. It gave no precipitate with an aqueous solution of sulfur dioxide. When heated in a sealed tube at 100° C. for four days, it became slightly viscous and colored and the refractive index rose to 1.4910 (26° C.), but there was no evidence of the formation of a rubber, as it gave no precipitate when alcohol was added.

TABLE VIII
DIMERIC PRODUCTS FROM DIMETHYLBUTADIENE

Substance	Boiling Point, ° C.	Refractive Index (n_D)
Oil from polymerization at 85° C. (<i>supra</i>)	Approx. 80 (10 mm.)	1.4775 (25° C.)
Oil from polymerization at 145° C. (<i>supra</i>)	198-200 (748 mm.)	1.4799 (21° C.)
Lebedev's compound	205 (750 mm.) 85 (13 mm.)	1.47716 (19.7° C.)
Aschan's compound	200.5-201.3 (760 mm.) 87 (12 mm.)	1.47915
Richards' compound	205 (760 mm.)	1.47786 (25° C.)

In another experiment 100 cc. of pure dimethylbutadiene was heated at 145° C. for 12.5 hrs. and the oily polymer isolated. After purification the oil gave no precipitate with sulfur dioxide solution. The oil yielded a sharply boiling fraction, 198-200° C. (748 mm.), n_D^{21} 1.4799.

The oil obtained in the experiments above is clearly essentially the same as the dimeric oil (dimethyl dipentene) isolated by Lebedev^{17,21} and by Aschan,^{1,3} from the polymerization products of dimethylbutadiene, and by Kondakov¹³ and Richards²⁹ from the decomposition products of dimethylbutadiene rubber, as Table VIII shows,

Effect of Temperature and Time on the Polymerization.—Samples of dimethylbutadiene were heated in glass tubes sealed at atmospheric pressure for different periods of time at temperatures of 45°, 85°, and 145° C. The yields of oily dimers and of rubber were obtained in a similar way to that used in the corresponding experiments with isoprene. The results have been summarized in Table I.

In all the experiments with dimethylbutadiene recorded in Table I the tubes used were of the same size (105 cc.) and contained the same volume of diene (50 cc.). The total volume in each experiment at 85° and 145° C. was 100 cc.; in the experiment at 45° C., 250 cc., and in the experiment at room temperature, 1000 cc. A further experiment, in which the ratio of air to diene was higher than in the

TABLE IX
CHANGE IN REFRACTIVE INDEX AND DENSITY WITH THE POLYMERIZATION OF DIMETHYLBUTADIENE

Time at 85° C., Hrs.	Refractive Index, n_D^{25}	Density, d_4^{25}	Rubber Formed, %
0	1.4367		
12	1.4420	0.7335	
24	1.4435	0.7372	
72	1.4464	0.7397	8.3 (found)
127	1.4486	0.7457	11.2 (found)
186	1.4500	0.7469	
372	1.4540	Too viscous	19.82 (calcd.)
550	1.4590	Too viscous	25.5 (calcd.)
578	1.4590	Too viscous	

above experiments, showed *inter alia* that the proportion of air to diene influences the rate of polymerization. In this experiment the tubes were 250 cc. in volume and contained 75 cc. of diene. The total volume of diene used was 375 cc. After 120 hrs. at 85° C. the yield of rubber polymer was 18.3 per cent.

Change of Refractive Index with Polymerization of Dimethylbutadiene.—Samples of 5 cc. of the diene were heated in sealed tubes of 15-cc. capacity for various periods at 85° C. and the refractive index and density of the total product was measured in each case. As the previous experiments have shown that only a small proportion of dimer is formed at 85° C. and that the main polymeric product is methyl rubber, it was possible to calculate the percentage of rubber formed at any time with fair accuracy. According to Macallum and Whitby²² the refractive index of methyl rubber is 1.5250 (at 20° C.), and that of the monomer from which it was prepared 1.4377 (at 20° C.). The change in refraction for 100 per cent polymerization is thus 0.0873. The monomer used in the experiments recorded in Table IX had n_D^{25} 1.4637.

TABLE X
TIME OF FLOW OF SOLS (0.8544 G./25 CC. BENZENE) OF FRACTIONS OF METHYL RUBBER

Fraction No.	1	2	2a	2b
Time of flow, sec.	55.4	72.1	67.8	81.3

In the following experiment the effect of air on the rate of polymerization was again observed. A quantity (10 cc.) of dimethylbutadiene was sealed in each of two tubes of 25-cc. capacity. One tube was sealed in the ordinary way and the other while the tube was cooled with solid carbon dioxide and ether and it was evacuated to 10 mm. The two were heated for 46 hrs. at 85° C. The refractive index of the contents was measured, with the following results: n_D^{26} of liquid in tube filled with air, 1.4440; n_D^{26} of liquid in tube sealed under reduced pressure, 1.4420; n_D^{25} of original diene, 1.4367.

TABLE XI
 VISCOSITY AND MOLECULAR WEIGHT OF DIMETHYLBUTADIENE RUBBER SAMPLES

Sample, Time and Temperature of Polymerization	Viscosity		Molecular Weight	
	Concentration G./20 Cc. Benzene	Relative Viscosity, Benzene = 1	Concentration G./20 Cc. Benzene	Mol. Wt.
(a) 101 hrs. at 85° C.	0.0862	1.24	0.2121	1443
	0.1881	1.53	0.5042	2110
	0.3231	1.96	0.7700	3400
	0.5161	2.80		Mean, 2318
	0.6677	3.69		
(b) 154 hrs. at 85° C.	0.0819	1.27	0.2230	1973
	0.2632	1.87	0.6788	3982
	0.3181	2.15	0.6713	4017
	0.4974	2.93	0.8597	4067
	0.6713	3.82		Mean, 3345
	0.6788	3.83		
	0.7147	4.11		
	0.8088	4.64		
	0.8597	5.08		
	0.9076	5.36		
(c) 250 hrs. at 85° C.	0.2121	1.78	0.2615	2402
	0.3270	2.25	0.6971	4645
	0.4600	3.00		Mean, 3524
	0.6454	3.93		
	0.6971	4.55		
	0.8143	5.17		
	0.8990	6.38		
(d) 900 hrs. at 85° C.	0.1529	2.49		
	0.2501	3.49		
	0.4830	7.19		
	0.6770	9.21	0.6770	3206
	0.6811	10.86		
	0.8721	13.20	0.8721	3760
				Mean, 3483
(e) 12.5 hrs. at 145° C.	0.2363	1.41	0.6804	2100
	0.4537	1.81	0.6885	2175
	0.6804	2.30		Mean, 2138
	0.6885	2.34		
	0.8625	2.84		
(f) 2628 hrs. at 45° C.	0.2418	1.53	0.2418	529
	0.4489	2.06		
	0.5255	2.24		
	0.6883	2.76	0.6883	1923
	0.7315	2.79	0.7315	2102
	0.8570	3.05	0.8570	2294
(g) 1920 hrs. at room temp.	0.2435	1.31	0.6838	1700
	0.4705	1.62	0.6612	1799
	0.5345	1.72	0.6922	2278
	0.6305	1.87		Mean, 1926
	0.6813	1.99		
	0.7477	2.11		
	0.7961	2.23		
	0.9031	2.33		

Heterogeneity of Dimethylbutadiene Rubber.—Methyl rubber (5.5 g.) was dissolved in 50 cc. of pure benzene, and there was added a mixture of 80 parts of absolute alcohol and 20 parts of benzene until a faint turbidity appeared. On standing overnight, the mixture separated into two layers, the upper one being quite fluid and the lower one very viscid. The layers were separated and the polymer precipitated from each by the addition of absolute alcohol. This gave Fraction 1 and Fraction 2, the latter being the larger. The products were carefully

dried *in vacuo*, and the viscosity of a sol prepared from a portion of each was measured. The balance of Fraction 2 was redissolved in benzene and separated into two sub-fractions (2a, 2b) by precipitation with the alcohol-benzene mixture. The viscosity of sols prepared from the fractions was measured. The results are shown in Table X.

Unsaturation of Dimethylbutadiene Rubber.—The polymer prepared by heating dimethylbutadiene at 85° C. for 101 hrs. was purified by repeated solution in benzene and precipitation with alcohol and finally by prolonged drying *in vacuo*. The unsaturation of the product was determined by the method of Kemp.¹¹ The iodine numbers obtained were 309.1, 307.8, 298.6, and 297. These numbers correspond sufficiently well with the calculated value of 309.1 to show that the polymer contains, as nearly as such a method of analysis can decide, one double bond for each (C₆H₁₀) unit.

Viscosity and Molecular Weight of Dimethylbutadiene Rubber Samples.—The rubber-like residues left after removing unchanged diene and oily polymers in the above experiments were purified by precipitation as in the case of the corresponding isoprene rubber samples, and determinations were similarly made of the molecular weight of the samples and the viscosity of their sols. The results are shown in Table XI. Mean values for the molecular weights have been recorded in Table I.

Change in Viscosity of Sols on Keeping.—It was found that sols of dimethylbutadiene rubber showed a marked decrease in viscosity when kept. In Table XII are recorded measurements made after keeping a number of sols in the dark for various periods, the volume of each sol being 20 cc. and that of the containing bottles 50 cc. (cf. Fig. 2).

TABLE XII
CHANGE IN VISCOSITY OF SOLS OF DIMETHYLBUTADIENE RUBBER ON KEEPING

No.	Concentration G./20 Cc. Benzene	Time of Flow (Sec.) at 30.1° C.		
		8 Days after Preparation	17 Days after Preparation	33 Days after Preparation
1	0.8990	155.4	115.0	81.6
2	0.8143	126.2	98.9	73.6
3	0.6454	95.8	78.4	61.6
4	0.4600	73.2	63.4	51.7
5	0.3270	55.0	50.0	43.9
6	0.2121	43.3	41.2	37.7

NOTE: Time of flow of pure benzene: 24.4 sec.

As the above data show, the higher the original viscosity the greater is the decrease; further, the rate of decrease falls as time goes on.

TABLE XIII

No.	Concentration G./20 Cc. Benzene	Relative Viscosity at 30.1° C.		
		(a) Fresh Sol.	(b) After Keeping 53 Days	(c) After Recovering Rubber from (b) and Redissolving It
1	0.8088	4.65	2.38	2.40
2	0.7147	4.23	2.23	2.23

It was found that the change in the viscosity of the sols resulted from a permanent change in the polymer. Each of two sols which had been kept for 53 days was poured into absolute alcohol. As the precipitates would not coagulate, the mixture was evaporated at room temperature, and the product, which was sticky and entirely different from the originally tough, elastic material, was made up to the original concentration in fresh benzene. The viscosities of the solutions,

measured next day, agreed, not with the initial but with the decreased values, as the figures in Table XIII show.

The fall in viscosity is apparently due to oxidation; it could be prevented by the addition of dimethylaniline, as is shown in Table XIV in which are recorded the results with a sol of dimethylbutadiene rubber (obtained by polymerization at 45° C.) in benzene.

TABLE XIV

	Time of Flow, Sec.	
	Originally	After 34 Days
Without addition	49.2	40.1
With 0.0926 g. dimethylaniline in 20 cc. sol.	49.2	49.3

The behavior on vulcanization of some of the rubber polymers described herein will be dealt with in a forthcoming paper.

Addendum.—There has come to the authors' attention since the above was written a paper by T. Wagner-Jauregg³³ in which also the alleged formation of open-chain dimers on heating isoprene is traversed experimentally, with results in substantial agreement with those reported in the present paper. Following polymerization conditions given by Harries and conditions given by Ostromislenski, no open-chain dimeric product was formed. On heating isoprene at 85–90° C. for 4–5 days the main terpenic fraction had the following properties: b. p. 170–174° C.; $n_D^{21.5}$ 1.4730. It was not polymerizable on heating with sodium. The author regards it as identical with Aschan's dipene, but did not examine it for dipentene. On heating isoprene (160 cc.) with acetic acid (0.8 cc.) at 100° C. for six days the main fraction had the following properties: b. p. 172–174.5° C.; n_D^{17} 1.4754; d_4^{19} 0.8454. This material, too, which corresponds to Harries' product, is also regarded as being identical with Aschan's diprene. The author remarks that "diprene" is probably a mixture of closely similar hydrocarbons. The author points out that the recent recognition of the frequent occurrence of the isoprene skeleton in nature, not only in terpenes, sesquiterpenes, and rubber, but also in carotinoids, squalene,* phytol, bile acids, cholesterol, hop resin acids, confers added interest on the question of the modes of dimerization of isoprene.

* Cf. References 35 and 36.

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Studies of Polymers and of Polymerization

VI. The Vulcanization of Methyl Rubber

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Abstract

Samples of synthetic rubber prepared by the polymerization of dimethylbutadiene at room temperature and at 45° C., respectively, were subjected to vulcanization tests in comparison with natural rubber. In an accelerated gum stock containing 3% sulfur the cold polymer gave at best vulcanized products less than one-third as strong and only about one-third as extensible as natural rubber; the heat polymer gave products as extensible but only one-tenth as strong as natural rubber. The incorporation of carbon black greatly increased the strength of the synthetic rubbers, rendering both about one-half as strong as natural rubber in a similar stock. The vulcanized synthetic rubbers were less "snappy" than natural rubber at room temperature. Increase of temperature improved their speed of retraction, but seriously reduced their breaking strength. Products from the cold polymer showed a greatly increased stiffness and strength at 5° C. as compared with room temperature, and at about 1° C. were non-retractible. In general the synthetic rubbers were much more sensitive than natural rubber to change of temperature. A 50:50 mixture of the heat and cold polymers was also subjected to tests.

The ability of 2,3-dimethylbutadiene to undergo polymerization to a rubber-like product was first observed by Kondakov.⁸ When, during the War, the manufacture of synthetic rubber on a large scale was, owing to the exigencies of the time, undertaken in Germany, the polymerizant chosen was 2,3-dimethylbutadiene, and, since this is a methyl homologue of isoprene, the polymerizant of natural rubber, the rubber produced was designated methyl rubber. About 2350 tons of methyl rubber were manufactured at Leverkusen during the War, and at the close of the War there were in course of erection two additional plants for its manufacture with a joint capacity of 8000 tons a year.^{4, p. 214, 6} Accounts of the German wartime experience with methyl rubber have been given by Gottlob,⁵ Duisberg,³ F. Hofmann,⁶ Burgdorf¹ and Weil,¹⁰ but the descriptions of the properties of methyl rubber given by these writers are in general terms only, and, with the exception of Pohle's work on the colloidal behavior of this rubber,⁹ there is in the literature a lack of any numerical or other exact data concerning the properties of methyl rubber, especially after vulcanization, which would enable them to be compared in quantitative terms with the properties of natural rubber. In view of this lack and of the renewed interest in synthetic rubber which has been excited by the discovery of a synthetic rubber from 2-chlorobutadiene² the present work was carried out.

In an earlier paper of this series data have been given on the rate of polymerization of dimethylbutadiene under the influence of heat and on the molecular weight and viscosity of the resulting methyl rubber.¹² In the present paper are recorded experiments on the vulcanization of methyl rubber and the properties of the vulcanized products compared with the properties of vulcanized natural rubber. The experiments were confined to soft vulcanized rubber, partly because the statements in the literature relating to the German wartime experience are more definite in regard to the preparation of hard than in regard to the preparation of soft rubber from methyl rubber, and partly because the quantity of material available was

limited. There was used in the experiments methyl rubber of two types, namely, (a) rubber formed by spontaneous polymerization at room temperature; (b) by polymerization at 45° C. These are referred to as the cold polymer and heat polymer, respectively, and may be compared roughly with the *H* (hart) and *W* (weich) rubbers formerly manufactured in Germany by polymerization at 30° and 70° C., respectively.

In the experiments carried out, the methyl rubbers obtained by cold and by hot polymerization and also a 50:50 mixture of these products were compared with natural rubber in a gum stock and in a carbon black stock. The influence of temperature on the tensile strength, elongation, and retractive power of the vulcanizates was also studied.

It was found that in a gum stock the cold polymer gave, at the best cures, vulcanized products less than one-third and the heat polymer not more than one-tenth as strong as were given by natural rubber. The vulcanized cold polymer suffered rupture at a low elongation, the ultimate extension being only about one-third that of natural rubber. The vulcanized heat polymer, on the other hand, though, as already stated, far weaker than vulcanized natural rubber, was almost as extensible as the latter (see Table I).

The incorporation of carbon black exercised a much more striking effect in methyl than in natural rubber, particularly in the case of the heat polymer. The addition of 25 parts of this ingredient to the gum stock raised the maximum tensile strength from 28.2 to 166.5 kg. per sq. cm. in the case of the heat polymer; from 86.4 to 161 kg. per sq. cm. in the case of the cold polymer; and only from 293 to 349 kg. per sq. cm. in the case of natural rubber. The profound effect of carbon black on the tensile properties of methyl rubber is shown, not only by the increase in the ultimate tensile strength just noted, but also by the marked stiffening of the stock. The cold polymer, already somewhat stiffer than natural rubber in the gum stock, was, by the addition of carbon black, rendered far stiffer than natural rubber in a similar stock, the load required to extend to twice the original length samples cured to the point of maximum tensile strength being 54.2 and 19.7 kg. per sq. cm. in the two cases, respectively (see Table I). Increase in the carbon black from 25 to 50 parts did not, in experiments with the cold polymer, further increase the ultimate tensile strength, although it stiffened the rubber compound, as is indicated in Table I by the figures for T_2 (load producing an extension of twice the initial length). The effect of carbon black in raising the tensile strength of synthetic rubber has lately been mentioned in the patent literature.⁷

In view of the relatively small influence of carbon black on natural rubber compared with its great effect on the soft heat polymer, it may be surmised that in natural rubber only a very small fraction, if any, of it is soft material in a relatively low state of polymerization.

As other papers^{13,14} in this series show, high polymeric products are in general markedly heterogeneous, and consist of mixtures of polymeric molecules representing a range of molecular weights. Methyl rubber produced by heat polymerization was shown to be thus heterogeneous,¹² and it seems fair to assume that the cold polymer too is heterogeneous. Further, it has been shown that, other things being equal, the lower the temperature at which the polymerization of a given polymerizant occurs, the higher is the mean molecular weight of the polymerizate. Hence it is probable that methyl rubber produced by polymerization at room temperature ("the cold polymer") has a higher molecular weight than methyl rubber produced by polymerization at 45° C. ("the heat polymer"). The behavior of the two materials toward solvents and swelling agents, as recorded in the experimental part, is in accord with this view. The heat polymer disperses much

more readily than the cold polymer; indeed the latter failed to disperse in all the liquids employed and it was in consequence impossible to determine its molecular weight.

In the case of polystyrene it has been established¹⁵ that the elastic properties of samples prepared in different ways depend on the molecular weight. Material obtained by the spontaneous polymerization of styrene at room temperature has a much higher molecular weight than material obtained by polymerization at, *e. g.*, 140° C., and, correspondingly, disperses less readily in solvents and has different elastic properties. The cold-polymerized material has a greater strength and smaller extensibility than the heat-polymerized material. This is analogous to the behavior of the vulcanized products from the samples of methyl rubber obtained in the cold and at an elevated temperature.

It may provisionally be considered that in order to secure optimum elastic properties in an elastic polymer, *i. e.*, high tensile strength together with high extensibility, it is necessary that the polymeric molecules present shall extend over a certain optimum range and shall be present in appropriate proportions. In order to secure stress-strain relations similar to those exhibited by natural rubber, it would seem that, speaking broadly, there should be present a suitable proportion of material in a relatively low state of polymerization in order to render the material readily extensible on the application of small loads; a suitable proportion in an intermediate state of polymerization and responsible largely for the intermediate part of the stress-strain curve, and a suitable proportion in a high state of polymerization which confers tenacity, enables high loads to be sustained with little deformation, and is responsible largely for the last part of the stress-strain curve.

In view of considerations such as the foregoing, experiments were carried out on the vulcanization of a mixture of equal parts of the cold and heat polymers. The former polymer, representing material in a higher state of polymerization, yields on vulcanization alone a product of relatively good strength but poor extensibility; the latter, representing material in a lower state of polymerization, a product of poor strength but good extensibility. The product from the 50:50 mixture was found to have almost as good an extensibility as the heat polymer alone and a tensile strength between that of the heat and cold polymer. The quantity of material available did not permit of experiments on mixtures in other proportions, but such further experiments would probably be instructive and are to be desired.

The vulcanized products from methyl rubber not only had a markedly lower tensile strength than those from natural rubber but much poorer "nerve;" that is to say, when allowed to recover under no load after being extended, they retracted with much less "snap" than natural rubber. This was particularly so with the cold polymer, which retracted very sluggishly and was decidedly loggy. The figures for "set" given in Table I represent the residual extension in per cent half an hour after the specimens had been stretched to the point of rupture. These figures do not well reveal the lack of "snap" in the synthetic rubber. The latter is, however, well shown by the figures given in Table II for the residual set left at intervals up to four minutes after stretching specimens to 150 per cent and then allowing them to retract under no load. It was observed that, when warmed, the specimens of methyl rubber largely lost their sluggishness. This is shown by the data given in Table II on the retraction of the specimens when allowed to retract at 45° C. after being stretched 150 per cent at that temperature. At 70° C. the samples of vulcanized methyl rubber retracted with almost as good a "snap" as natural rubber, but, as data in Table III show, were lacking in strength.

The effect of introducing small proportions of plasticizers into the stiff carbon black stock from the cold polymer was examined. It was found to increase somewhat the ultimate extension (Table I) and to improve, but not strikingly, the speed of retraction (Table II).

The tensile properties of methyl rubber vulcanizates were determined not only at room temperature, but also at a reduced temperature (5° C.) and at elevated temperatures (37° and 70° C.). (See Table III.) It was found that all the specimens of vulcanized methyl rubber were much more sensitive to temperature changes than was natural rubber. The heat polymer was particularly sensitive to fall of temperature and the cold polymer to rise of temperature. Reduction in the temperature from 20° to 5° C. increased the tensile strength of the gum vulcanizate from the cold polymer from 28.2 to 181 kg. per sq. cm. Increase in the temperature from 20° to 37° C. reduced the tensile strength of the gum vulcanizate from the heat polymer from 68.4 to 10.9 kg. per sq. cm. Natural rubber, on the other hand, showed little stiffening when the temperature was lowered to 5° C. and relatively little softening when it was raised to 37° C., the figures for tensile strength at 20°, 5°, and 37° C. being 285, 272, and 219 kg. per sq. cm., respectively. Even at 70° C. the natural rubber retained a substantial part of its tensile strength, especially when it was compounded with carbon black, whereas methyl rubber was extremely weak. Thus, for example, the gum polymerizate from the cold polymer, which at 20° C. had a tensile strength of 68.4, had at 70° C. a tensile strength of only 2.4 kg. per sq. cm.

In conclusion it may be remarked that methyl rubber is certainly susceptible to being influenced in its rate of vulcanization by an accelerator such as is effective with natural rubber. Several attempts to vulcanize a simple mixture of 100 parts methyl rubber (cold polymer), 5 parts sulfur, and 5 parts zinc oxide at 133° C. were entirely unsuccessful. The mixture was quite uncured, and stuck to the mold after seven hours' heating. On the other hand, as the data in Table I show, a mixture of the rubber containing only three parts of sulfur but in addition one part of an accelerator of the dithiocarbamate class was well vulcanized after 30 mins.' heating at 110° C. It may be noted further that the methyl rubbers are much less susceptible to overcuring than is natural rubber. Thus, for example, in the gum stock used natural rubber is well cured in 15 min. at 110° C. and overcured in 20 min. or less at 133° C., whereas methyl rubber (cold polymer) gives similar results on the one hand in 30 min. at 110° C. and on the other hand in 80 min. at 133° C.

Gottlob⁵ has stated that in the early experiments with methyl rubber it was found that vulcanization in the presence of sulfur and fillers only led to combination of not more than a few tenths per cent of sulfur, but when heated with 10 per cent of sulfur for one hour at 152.4° C. (4 atm. steam pressure) in the presence of piperidine "a few per cent of sulfur were combined." In the present experiments on the vulcanization of methyl rubber in a stock containing a very strong accelerator combination, *viz.*, a dithiocarbamate with zinc oxide, it was found that the rate of combination of sulfur was of the same order of magnitude as, albeit a little slower than, with natural rubber, and that the heat polymer combined with sulfur a little more slowly than the cold polymer. Data are given in Table V.

Vulcanized methyl rubber was found to imbibe swelling agents to a similar extent to natural rubber (Table IV).

Experimental

The methyl rubber used in these experiments was obtained as follows. Di-methylbutadiene was heated in sealed glass tubes at 45° C. for 186 days. This caused the polymerization of a part of the diene and yielded a viscous liquid. The

contents of the tubes were then allowed to stand at room temperature for four summer months, and when the tubes were then examined it appeared the whole of the contents had undergone polymerization. Probably the rapidity with which the diene, still unchanged at the end of the heating period, had polymerized at room temperature was due to "seeding" by the polymer already formed. The contents of the tubes consisted of two clearly distinct parts, namely, a clear, elastic lower portion representing the result of heat polymerization and an upper portion which almost filled the rest of the tube and consisted of the typical white "cauliflower" masses characteristic of cold-polymerized dimethylbutadiene. The heat polymer was about 28 per cent of the whole. The tubes were allowed to stand for three and one-half years in all; they were then opened, the two portions were separated and were then employed in the following experiments with as little delay as possible, being kept in an atmosphere of carbon dioxide in the meantime.

Since both the "heat" and the "cold" polymers appeared to be susceptible to oxidation (a few days' exposure to the air caused them to become sticky) an anti-

TABLE I
PHYSICAL PROPERTIES OF NATURAL AND METHYL RUBBER AT 20° C. IN GUM AND CARBON BLACK STOCKS

Cure	T ₂	T ₅	Gum stock*		E _B	Set	Cure	Gum stock + 25 pt. carbon black + 1.5 pt. stearic acid				
	T ₂	T ₅	T ₄	T _B				T ₂	T ₅	T _B	E _B	Set
<i>I. Smoked Sheet</i>												
5'/110° C.	3	15'/110° C.	9.2	85.6	155	606	12.3
10	6.2	19.9	33.7	168	875	10.5	20	13.1	133.5	251	636	18.9
15	10.7	41.2	85.3	274	834	16.4	25	17.5	196	273	580	25.8
20	12.2	62.8	134.0	282	754	22.5	30	19.7	194	349	650	30.3
25	15.1	82.8	172	277	709	24.7	30	19.3	193.5	346	648	39.0
30	16.1	96.8	194	293	710	25.4						
20'/133° C.				24	206							
40				16.4	164							
60				15.5	161							
<i>II. Methyl rubber (heat polymer)</i>												
20'/110° C.		10.9		16.8	788	2.2	40'/110° C.	93.2	150.7	611	10.0	
30		17.1		21.5	610	1.0	60	150.0	166.5	531	12.3	
40		26.2		28.2	509	1.0						
20'/133° C.		..		28.2	365	1.1						
<i>III. Methyl rubber (cold polymer)</i>												
30'/110° C. 26.6				77.6	293	2.7	20'/133° C.	55.4		155	340	9.2
20'/133° C. 25.0				86.4	243	1.1	20	54.2		161	302	10.0
40		25.4		68.4	228	1.1	40	90.0		153	278	10.5
60		24.6		81.0	241	1.0						
80		22.0		76.1	245	1.2						
<i>Gum stock + 50 carbon black + 1.5 stearic acid</i>												
							20'/133° C.	101		129	258	12.6
							40	133		156	259	22.4
							60	123		130	217	19.1
							(+ 5% plasticizer) 20'	87		153	350	16.9
							(+ 10% plasticizer) 20'	65		122	355	15.7
<i>IV. Methyl rubber (heat and cold polymers, 50:50)</i>												
30'/110° C.	17.5			33.3	610	2.7						
40	31.0			42.0	535	2.7						
20'/133° C.	..			51.0	400	2.2						

* Gum stock: rubber, 100, sulfur, 3, zinc oxide, 5, anhydroaldol- α -naphthylamine, 1, piperidiniumpentamethylene dithiocarbamate, 1.

Tensile strength given in kg. per sq. cm.; elongations and set in per cent. T₂, T₅, T₆ = tensile strength at 200, 500, and 600% elongation, respectively. T_B = tensile strength at break; E_B = per cent elongation at break.

oxidant was added to all compounded stocks. Anhydroaldol- α -naphthylamine proved to be effective in this connection. It prevented oxidation of methyl rubber in compounds kept uncured for at least six weeks.

On the mill the behavior of the cold polymer was noticeably different from that of natural rubber. It was at first crumbly and fell through the rolls, but by continued treatment on hot rolls it became more plastic, and eventually there was obtained a sheet, which, however, was leathery and devoid of tackiness. The cold polymer took about twice as long to mill as natural rubber. The heat polymer broke down on the mill quite readily and in a similar manner to natural rubber, but a sheet of compounded stock from the heat polymer was noticeably less tacky than a corresponding sheet from natural rubber.

Vulcanization was carried out in molds designed to produce molded ring test pieces. These molds, which were designed by D. F. Stedman, and will shortly be described by him in this JOURNAL, do not involve any waste of rubber in producing test pieces and are well adapted for working with small quantities of material. Strips about 14 cm. long and weighing about 1.5 g. were cut from the milled sheets and placed in the ring molds. The latter were then placed in a small hydraulic press and a pressure of 1000–4000 lb. per sq. in. applied for 10–15 min. in order to make the strips fit the molds perfectly. Vulcanization was then brought about by heating the molds in a constant-temperature bath at either 110° or 133° C. for various periods of time. The molded test rings thus secured were of standard diameter (44.5 mm.) and thickness (3.15 mm.) and of a height which varied slightly according to the amount of rubber used but was approximately 2.5 mm. The tensile strength and elongation of the test pieces were determined 24 hours after curing by means of a Schopper machine which gave an autographic load-strain curve. Set was determined by measuring the length of the test pieces 30 min. after rupture. The set thus determined is substantially all permanent set, as measurements of test pieces several days after rupture did not indicate any further retraction, and as heating to 68° C. for five minutes also failed to produce further retraction.

The results are given in Table I—the figures given for the stocks containing natural rubber represent the mean of the results for three test pieces in each case; those for the methyl rubber stocks in most, but, owing to the limited amount of material, not all cases represent the mean of the results for two test pieces.

The plasticizer used in certain stocks as noted in the table was methyleyclohexyl adipate.

Retraction of Methyl Rubber.—The results given in Table II show the rate of retraction at room temperature (20° C.) and at 45° C. when samples 5 cm. long of various vulcanized stocks from methyl rubber are stretched 150 per cent for three minutes and then allowed to retract under no load. For comparison, a properly cured and an undercured sample (see Table I) of natural rubber are included. It will be observed that the slow rate of retraction at 20° C. of the methyl rubbers in a gum stock is similar to that of the badly undercured sample of natural rubber.

Effect of Temperature on the Physical Properties of Methyl Rubber.—It has already been pointed out that, although vulcanized methyl rubber, especially if prepared from the cold polymer, is sluggish at room temperature, it becomes readily retractible at elevated temperatures, and at 70° C. or more has a "snap" similar to that of vulcanized natural rubber. Furthermore, if vulcanized methyl rubber is stretched at temperatures below its elasticity temperature, say, 1° C., it will remain stretched and will not retract until warmed. Its behavior in this respect is similar to that of raw rubber. In order to study more closely the effect of temperature on

methyl rubber, in comparison with its effect on natural rubber, a series of tensile measurements was made at temperatures of 5°, 20°, 37°, and 70° C.

TABLE II
RATE OF RETRACTION OF VULCANIZED NATURAL AND METHYL RUBBER (GUM STOCK AS GIVEN IN TABLE I)

Specimens Extended 150 Per Cent for Three Minutes and Allowed to Retract

At 20° C.

Sample	Cure	0.25 Min.	0.75 Min.	Set after: 2 Min.	4 Min.	30 Min.
Natural rubber	5'/110° C.	8.0	5.6	3.0	2.2	2.0
Natural rubber	20'/110° C.	2.0	1.2	1.0	1.0	1.0
Heat polymer	30'/110° C.	10.0	4.0	1.0	1.2	0.4
Cold polymer	40'/133° C.	9.0	6.0	1.0	1.0	1.0
Cold polymer + 25 pt. C black	40'/133° C.	22.2	13.0	7.0	5.0	2.4
Cold polymer + 50 pt. C black	20'/133° C.	56.0	29.0	15.0	9.9	4.8
Same + 10 pt. plasticizer	20'/133° C.	30.0	16.0	9.0	7.2	3.4
Unvulcanized heat polymer		50.0	35.0	24.0	16.0	10.0

At 45° C.

Heat polymer	30'/110° C.	10.0	2.4	1.6	1.6	1.6
Cold polymer	30'/110° C.	6.0	2.0	1.0	1.0	1.0
Cold polymer + 25 pt. C black	40'/133° C.	3.6	2.2	1.2	0.4	0.4
Cold polymer + 50 pt. C black	20'/133° C.	8.0	5.6	3.6	2.6	2.6
Same + 10 pt. plasticizer	20'/133° C.	9.0	4.4	2.8	1.6	1.2

For the purpose of these measurements there was made and mounted on a Schopper testing machine a constant-temperature bath which permitted the specimens to be immersed in water at the desired temperature along their entire length up to the point of rupture. The bath consisted of a long rectangular metal tank, 34 by 3.5 by 4 in., with a hole in the bottom to allow the passage of the rod carrying the lower grip. By means of a packing gland of oil and graphite, the hole was made water-tight. Electrically regulated immersion heaters were inserted in the tank, and the water was stirred by means of a stream of air, which proved more satisfactory than a mechanical stirrer. Repeated tests with ordinary rubber showed that the effect of immersion in water during the short period of the test was negligible. The specimens were immersed without tension for a short time in the water before stretching, in order to allow them to come to temperature. Grips for holding the ring-shaped test pieces presented a little difficulty at first, because it was found that rotation of the test piece was essential for proper results. The required rotation was secured by using at each end of the testing machine gap two ball-bearing pulleys spaced horizontally. The pulleys, which were grooved, were about 1.4 cm. in diameter and about 3 cm. between centers. Using this arrangement, it was found that the test piece rotated as tension was applied, and there was no indication of the rubber being cut at the point of contact. Substantially similar results were obtained in comparative tests using these pulleys in the bath, and then substituting the standard mechanically rotated pulleys of the Schopper machine and carrying out tests at the same temperature in the air.

Selected cures of the same series of stocks (a gum stock and a carbon black stock) as had already been tested at room temperature (Table I) were put through tests at the other temperatures mentioned. The results are given in Table III.

Behavior toward Swelling Agents.—In benzene and in chloroform the cold polymer only partly dissolved after seven days and left a large swollen residue; the

TABLE III
THE EFFECT OF TEMPERATURE ON THE STRESS-STRAIN PROPERTIES OF NATURAL AND METHYL RUBBER

Heat Polymer	Cold Polymer	Heat and Cold Polymers (50:50)	Heat Polymer + 25 Pt. Carbon Black	Cold Polymer + 25 Pt. Carbon Black	Smoked Sheet	Smoked Sheet + 25 Pt. Carbon Black
<i>Temperature, 5° C.</i>						
Cure 40°/110° C. 60°/110° C.		20°/133° C.	40°/133° C.	20°/110° C.	30°/110° C.	
<i>T_s</i> 33.1	36.0	86.6		22.3	72.2	
<i>T_b</i> 181	64	161	138	131	264	
<i>E_b</i> 516	393	411	230	272	350	
Set 4.5	6.1	4.7		622	583	
				20.2	35.0	
<i>Temperature, 20° C.</i>						
Cure 40°/110° C. 30°/110° C. 40°/133° C.		40°/110° C. 60°/110° C.	40°/133° C.	20°/110° C.	30°/110° C.	
<i>T_s</i> 19.2	25.4	18.5	32.0	18.6	48.0	
<i>T_b</i> 26.2	77.6	51.0	150.7	80.8	194	
<i>E_b</i> 28.2	293	400	611	285	347	
Set 1.0	2.7	2.2	10.0	694	649	
				18.6	34.4	
<i>Temperature, 37° C.</i>						
Cure 40°/110° C. 60°/110° C. 40°/133° C.		40°/110° C.				
<i>T_s</i> 8.1	6.8	5.0		17.1	38.7	
<i>T_b</i> 14.8	13.2	10.9	55.0	48.5	140	
<i>E_b</i> 360	317	280	230	219	285	
Set 0.9		3.4	5.6	712	668	
				19.5	43.5	
<i>Temperature, 70° C.</i>						
Cure 40°/110° C.	40°/133° C.	20°/133° C.	40°/110° C. 60°/110° C.	40°/110° C.	20°/110° C. 30°/110° C.	
<i>T_s</i>		15.3	25.4	25.9	15.1	28.8
<i>T_b</i>		5.4	23.1	26.3	36.1	84.9
<i>E_b</i> 230	2.4	191	380	306	106.5	185.5
Set 1.1	1.0	1.1		4.5	680	685
					21.4	

Note: Stock: rubber or methyl rubber, 100; sulfur, 3; zinc oxide, 5; anhydroaldol- α -naphthylamine, 1; piperidinium pentamethylene dithiocarbamate, 1.

heat polymer was nearly all dissolved after two days, although even after seven days there still remained a small undispersed residue. After seven days in ether, the cold polymer was slightly swollen but undissolved; the heat polymer had dissolved to the extent of nearly one-half. The cold polymer swelled in ethyl benzoate and in piperidine, but only a small portion had dissolved after seven days. Nearly one-half of the heat polymer dissolved in these liquids in two days, but it had not all dispersed after seven days. The above observations indicate the mean molecular weight of the cold polymer is markedly higher than that of the heat polymer, and that both materials are composed of a mixture of molecules in different states of polymerization.^{et. 11}

The swelling of samples of the methyl rubber and of natural rubber cured under similar conditions in the gum stock was measured with the results given in the following table.

TABLE IV
SWELLING OF VULCANIZED METHYL RUBBER, SYNTHETIC ISOPRENE RUBBER, AND NATURAL RUBBER

Samples Cured for 30 Min. at 110° C. in the Gum Stock Quoted in Table I

	Cold Polymer		Grams of Liquid Imbibed by 0.1 Gram				Synthetic Isoprene Rubber*	
	1 day	2 days	Heat Polymer		Natural Rubber		1 day	2 days
Benzene	0.330	0.3305	0.370	0.371	0.345	0.345	0.330	0.330
Petrolie ether	0.190	0.190	0.210	0.211	0.180	0.180	0.1735	0.175

* In this case isoprene polymer obtained by polymerization in emulsion was vulcanized for 40 min. at 110° C.

Vulcanization Coefficient.—Determinations of combined sulfur in comparable cured stocks gave the following results.

TABLE V
COMBINED SULFUR IN VULCANIZED METHYL AND NATURAL RUBBER

	Combined Sulfur as Percentage of Rubber	
	Cure, 30 Min./110° C.	Cure, 20 Min./133° C.
Natural rubber	3.09	3.11
Heat polymer	2.42	3.01
Cold polymer	1.89	3.05

Stock: Rubber, 100; S, 3; ZnO, 3; anhydroaldol- α -naphthylamine, 1; piperidini-umpentamethylene-dithiocarbamate, 1.

The total sulfur in the stock was 3.27 per cent (expressed on the rubber). Of this the accelerator contributes 0.27 per cent. Judging from the results for the natural rubber samples it would seem that about 0.17 per cent of sulfur from the accelerators remains extractable.

Acknowledgment

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⁶ Hofmann, *Mitteilungen aus dem schlesischen Kohlenforschungsinstitut des Kaiser-Wilhelm-Gesellschaft in Breslau*, **11**, 2, 235-248 (1925).

⁷ I. G. Farbenindustrie, French Pats. 655,217, 701,102 (1928, 1930).

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⁹ Pohle, *Kolloidchem.-Beihefte*, **13**, 1-60 (1921).

¹⁰ Weil, *Ind. Eng. Chem.*, **18**, 1174 (1926).

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¹³ Whitby and Katz, *J. Am. Chem. Soc.*, **50**, 1160 (1928).

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Isoprene and Rubber

Part 37. Homologous Polypranes

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I. Comparison of Homologous Polypranes

According to investigations by Staudinger and Fritsch¹ the hydrorubber obtained by the catalytic reduction of rubber at 270° is a high molecular paraffin hydrocarbon. Concurrently with this work, Pummerer and Burkard² were occupied with the reduction of rubber. They describe hydrorubber as an autooxidizable substance, an observation which has been shown to be incorrect.³ According to Pummerer and Koch,⁴ hydrorubber can be distilled in high vacuo without decomposition, and is a highly viscous oil having the composition (C₅H₁₀)₁₀. The hydrorubber obtained in this way is, however, according to experiments by Staudinger and Schaal⁵ highly decomposed by cracking.

Our concept⁶ of the constitution of hydrorubber and the products obtained from it by cracking is again confirmed by the preparation by Karrer, Stoll, and Stevens⁷ of two high molecular hydrocarbons with numerous methyl side chains. Like octomethyldotriacontane (C₄₀H₈₂) recently prepared by Karrer,⁸ hexahydrosqualene (C₃₀H₆₂)⁹ and tetramethylhexadecane (C₂₀H₄₂) prepared by Fischer,¹⁰ these new hydrocarbons are to be regarded as lower members of the series of paraffins with branched chains, whose end members are hydrorubbers. Accordingly, in this series of hydrocarbons (the polypranes), representatives from the lowest member, isopentane C₅H₁₂, to the highest member, a hydrobalata having the composition (C₅H₁₀)₇₀₀ and a molecular weight of about 50,000 are known.

Table I shows that the physical properties of these polypranes change in a regular way with increasing molecular weight, *e. g.*, the boiling point increases, the solubility in alcohol decreases, and the consistency of the substances changes. The lowest molecular products are thin liquids, the higher are viscous, becoming more viscous until at last the highest molecular hydrorubber has properties similar to rubber without being as elastic as the latter. Furthermore, the density increases in the expected way, *i. e.*, the number of chemically united carbon atoms in a unit volume increases with increasing molecular weight, whereas the number of large intermolecular atomic distances diminishes.

The products of the cracking of hydrorubber, which have already been described¹¹ and which have a double bond at the end of the chain on each molecule, have the same physical properties as the paraffin hydrocarbons with branched chains of the same molecular weight. The product of cracking with an average molecular weight of 440 resembles hydrosqualene, and the highest molecular product of cracking with an average molecular weight of 940 resembles tetrabixane. A hydrocarbon having the formula (C₅H₁₀)₁₀, which Pummerer and Koch considered a hydrorubber,¹² has accordingly different physical properties from true hydrorubber. It resembles dibixane, which is still fundamentally different from hydrorubber, as has also been shown by Karrer, Stoll, and Stevens.¹³

This comparison of the physical properties of different examples of hydrorubbers with branched chains again proves that hydrorubber must have a high molecular weight. This is one of the proofs of the high molecular character of rubber and of balata.

II. The Nature of Colloidal Solutions of Hydrorubber

Formerly it was the general opinion that micelles are present in colloidal solutions of rubber. In that case the colloidal particles of hydrorubber would also have to have a similar structure. Upon solution of hydrorubber, micelles rather than individual molecules would therefore be dissolved. This same idea in regard to the nature of a colloidal solution was supported by the publications of Meyer,¹⁴ who wrote as follows: "The main valence chains are united in definite lengths by cohesion, so that they do not separate in solution, but form micelles."

These ideas are erroneous, as is shown by the existence of this homologous series of polypranes. High molecular hydrobalata, whose solutions are colloidal, is united by continuous transposition with the individual members of the series, which dissolve in the normal way. The most important evidence of the molecular nature of the colloid particles of rubber and of balata lies, however, in the reduction of high molecular balata. It has been possible to reduce balata of a molecular weight of 51,000 to hydrobalata without changing the molecular weight. At the same concentration, solutions of hydrobalata show the same specific viscosity as solutions of balata. If the colloid particles have a micellar structure, then in such a deep seated chemical process as the destruction of the double bonds by reduction, the size of the micelles would have to be changed fundamentally, and this would lead to quite different properties of the solution.

III. Solubility of Homologous Polypranes

The great solubility of paraffins with branched chains in organic solvents, such as ether, benzene, chloroform, and carbon disulfide, is surprising, and in fact the high molecular members are also still readily soluble in the solvent named, though somewhat more slowly than the lower members. Great differences in solubility are evident only with alcohol and acetone, in which the higher members are insoluble (see Table I). In the case of paraffins with normal chains, on the contrary, the solubility in all solvents diminishes very rapidly with increase in the molecular weight, *i. e.*, with increase in the length of the chains, so that paraffins with 100 carbon atoms in the chain are extraordinarily difficultly soluble,¹⁵ and high molecular paraffins are wholly insoluble.¹⁶

A comparison of both series, as in Table II, shows that the solubility, like the melting point, of organic compounds depends not only on the size of their molecules but primarily on the structure itself and, in fact, substances with symmetrically formed molecules are more difficultly soluble and melt at a higher temperature than those which are unsymmetrically constructed. Structural isomers like stereoisomeric compounds may therefore show great differences in solubilities and melting points, whereas the differences in the boiling points are relatively slight. The volatility of an organic compound depends upon the size of the molecule, only if true homopolar compounds are considered. The Dunkel law of the additivity of molecular cohesion,¹⁷ upon which the micellar theory¹⁸ of Meyer is based, can be used in estimating only the volatility and not the solubility of organic compounds. This is evident by a comparison of tetrabixane and dimyricyl, two hydrocarbons which have approximately the same melting points. The paraffin with a normal chain has a high melting point and is very difficultly soluble, the paraffin with the branched chain is viscous and is readily soluble in benzene and ether.

The ready solubility of hydrorubber is accordingly a property which is common to all high molecular paraffins with branched chains.

TABLE I
HOMOLOGOUS PARAFFINS WITH BRANCHED CHAINS (POLYPYRANES)

Substance	Formula	Number of Chain Carbon Atoms ¹¹	Molecular Weight	Solubility in Absolute Alcohol	Appearance	Boiling Point	Density	$\eta_{sp}(7\%)$ in Benzene	$K_m = \frac{\eta_{sp}(7\%)}{M} \times 10^4$
Isopentane	C_5H_{12}	4	72	Easily soluble	Very thin liquid	B. p. ₇₆₀ 30°	d_4^{15} 0.628
2,6-Dimethyl-octane ¹	$C_{10}H_{22}$	8	142	Easily soluble	Thin liquid	B. p. ₇₂₄ 158°	d_4^{20} 0.730	<0.1	...
2,6,11,15-Tetramethylhexadecane ²	$C_{20}H_{42}$	16	282	Soluble	Liquid	B. p. ₁₁ 172°	d_4^{25} 0.7853	0.112	4.0
Perhydrosqualene ³	$C_{30}H_{62}$	24	422	Fairly soluble Soluble when hot	Liquid	B. p. ₁₀ 274°	d_4^{15} 0.8125	0.168	4.0
Cracked hydro-rubber ⁶	<i>ca.</i> $C_{31}H_{62}$	25	<i>ca.</i> 440	Fairly soluble Soluble when hot	Liquid	B. p. _{0.1} <i>ca.</i> 260°	0.16	3.6
Octamethyl-ditriacontane ⁴	$C_{40}H_{82}$	32	563	Liquid	B. p. _{0.3} 240°	d_4^{15} 0.823
Dibixane ⁵	$C_{48}H_{94}$	38	647	Slightly soluble when hot	Thick liquid	B. p. _{0.2} 270°	d_4^{21} 0.8287	0.277	4.3
Cracked hydro-rubber ⁶	<i>ca.</i> $C_{51}H_{104}$	<i>ca.</i> 53	<i>ca.</i> 940	Very slightly sol. when hot	Highly viscous	B. p. _{0.1} > 300°	0.32	3.4
Tetrabixane (decomposed) ⁵	<i>ca.</i> $C_{98}H_{140}$	<i>ca.</i> 56	<i>ca.</i> 970	Very slightly sol. when hot	Highly viscous	B. p. _{0.04} > 330°	0.396	4.1
Hydrorubber I ¹²	<i>ca.</i> $C_{114}H_{230}$	<i>ca.</i> 91	<i>ca.</i> 1600	Insoluble	Very highly viscous		0.48	3.0
Hydrorubber II ^{12,13}	<i>ca.</i> $C_{233}H_{462}$	<i>ca.</i> 260	<i>ca.</i> 4550	Insoluble	Very highly viscous Extraordinarily highly viscous		d_4^{15} 0.8610	1.2	2.6
Hemicolloidal hydrobalata ⁹	<i>ca.</i> $C_{500}H_{1002}$	<i>ca.</i> 400	<i>ca.</i> 7000	Insoluble			2.2 ¹⁰	...
Hydrorubber III ⁷ at 270° in soln.	<i>ca.</i> $C_{1200}H_{2402}$	<i>ca.</i> 960	<i>ca.</i> 17000	Insoluble	Hard, feebly elastic	Cracked on distillation	5.1	...
Hydrorubber IV ³ at 150° in soln.	<i>ca.</i> $C_{2100}H_{4202}$	<i>ca.</i> 1700	<i>ca.</i> 30000	Insoluble	Hard, feebly elastic		9.0	...
Hydrobalata ⁹ at 100° in soln.	<i>ca.</i> $C_{3200}H_{7002}$	<i>ca.</i> 2800	<i>ca.</i> 50000	Insoluble	Like rubber but not so extensible		15.4	..

(See footnotes on opposite page.)

IV. K_m - Constant of Polypranes

The specific viscosity of the hydrocarbons shown in Table I was determined in dilute benzene and tetralin solutions. The specific viscosity of solutions of like concentration increases with increase in the molecular weight by the same law as has been found for other homologous¹⁹ and polymeric²⁰ homologous compounds:

$$\frac{\eta_{sp}}{c} = K_m \times M$$

where c is the concentration of a base molar chain carbon atom in the base molar solution. In this series the base molecule is the C_8H_{10} group, and a base molar solution is therefore a 7 per cent solution. The K_m constant is approximately constant and is about 3.6×10^{-4} . With hydorrubbers it is somewhat smaller and averages 3.0×10^{-4} .²¹ However, these are not homogeneous compounds, but are mixtures of homologs, and such compounds do not show such exact relations.

With dibixane the K_m constant is larger than with the other hydrocarbons. However, this is not a homogeneous homologous polyprane, for dibixane contains on 8 methyl groups 38 chain carbon atoms, instead of only 32. Its molecule is therefore longer than that of a polyprane of the same molecular weight, and accordingly the viscosity of a 7 per cent solution is also proportionately higher.

TABLE II

Paraffins with Normal Chains	Melting Point	Boiling Point	Solubility in Benzene
$C_{20}H_{42}$	36.7°	B. p. (15 mm.) 205°	Easily soluble
$C_{30}H_{62}$	66.1°	B. p. (1 mm.) 235°	Soluble
$C_{60}H_{122}$	101°	> 300°	Difficultly soluble
ca. $C_{100}H_{202}$	> 100°		Insoluble
$C_{2000}H_{4002}$	Unknown
Paraffins with Branched Chains	Melting Point	Boiling Point	Solubility in Benzene
$C_{20}H_{42}$			
2,6,11,15-Tetramethyl-hexadecane	Liquid	B. p. (11) 172°	Miscible
$C_{30}H_{62}$			
Perhydrosqualene	Liquid	B. p. (10) 274°	Miscible
ca. $C_{60}H_{122}$			
Tetrabixane	Thick liquid	> 300°	Miscible
ca. $C_{114}H_{230}$			Easily soluble
Low molecular hydorrubber	Viscous	Cracked on distillation	
ca. $C_{2100}H_{4202}$			
High molecular hydro-rubber	Tough solid		Soluble

Footnotes to Table I

¹ Willstätter, Mayer, *Ber.*, **41**, 1478 (1908).

² Fischer and Löwenberg, *Ann.*, **475**, 204 (1929).

³ Tsujimoto, *Chem. Zentr.*, **1918**, I, 639.

⁴ Karrer, *et al.*, *Helvetica chim. acta*, **13**, 1084 (1920); **14**, 435 (1931).

⁵ Karrer, Stoll, and Stevens, *Ibid.*, **14**, 1194 (1931).

⁶ Staudinger and Fritsch, *Ibid.*, **5**, 785 (1922); Staudinger and Schaal, *Ibid.*, **13**, 1359 (1930).

Cracked hydorrubbers have the formula C_nH_{2n} , and contain one double bond per molecule.

⁷ Staudinger and Fritsch, *Ibid.*, **5**, 785 (1922); Staudinger, Geiger, Huber, Schaal, Schwalbach, *Ibid.*, **13**, 1334 (1930).

⁸ Staudinger and Feisst, *Ibid.*, **13**, 1361 (1930).

⁹ Unpublished experiments by Leupold.

¹⁰ Determined in tetralin solution.

¹¹ At the same time the approximate length of the molecules in A.U.

¹² Prepared at 270° without solution.

V. Viscosity Calculations

According to further investigators,²² very simple relations exist between the specific viscosity and the molecular weight of a hydrocarbon which consists of fiber molecules. These relations are evident if one compares the viscosities of chain-equivalent solutions, instead of base-molar solutions. The different hydrocarbons with branched chains such as polypranes, polystyrenes, etc., differ from one another in the type and size of the side chains. If the molecular weight of the hydrocarbons is divided by the number of carbon atoms in the molecule which are chain carbon atoms, the weight of all the side chains is distributed equally among all the carbon chain atoms. The weight thus obtained has been designated by us as the *chain-equivalent weight*. In homologous polymeric substances this chain-equivalent weight is obtained in a similar way from the weight of the base molecule and the number of carbon atoms in the form of chain carbon atoms in the base molecule.

Chain-equivalent weight of dibixane $\frac{647}{38} = 17$, where 38 is the number of the chain carbon atoms.

Chain-equivalent weight of hydrorubber $\frac{70}{4} = 17.5$.

Therefore with dibixane a 1.7 per cent solution, and with hydrorubber and perhydrosqualene, a 1.75 per cent solution is a chain-equivalent.

The following law applies to such solutions: *Chain-equivalent solutions of different hydrocarbons with fiber molecules of the same molecular weight in the same solvent (benzene or tetralin) have the same specific viscosity.* The specific viscosity of a dilute hydrocarbon solution may be calculated if the molecular weight is known and, in fact, on the basis of the following formula:

$$\eta_{sp(\text{equiv.})} = K_{\text{equiv.}} \times M = 0.85 \times 10^{-4} \times M.$$

In this way $\eta_{sp(\text{equiv.})}$ denotes the specific viscosity of a chain-equivalent solution. $K_{\text{equiv.}}$ is the constant for all hydrocarbons, regardless of the kind of side chain, and is around 0.85×10^{-4} for tetralin solutions. For benzene solutions it is somewhat higher, and is about 1.0×10^{-4} . Accordingly if the specific viscosity of hexahydrosqualene and dibixane are calculated by this law for chain-equivalent solutions, the values found agree approximately (see Tables III and IV). For

TABLE III
MOLECULAR WEIGHT DETERMINATION OF TETRABIXANE IN CAMPHOR (MICROMETHOD OF RAST)

Weight $\frac{W}{\text{in Mg.}}$	Quantity of Camphor L	Depression in Δ	$M = K \times \frac{W \times 1}{L \times \Delta}$	Average
0.505	7.120	3.1°	915	} 960 ²⁴
1.910	9.775	7.9°	993	
1.055	11.105	3.9°	975	

tetrabixane the value is considerably smaller, if the calculated molecular weight is used. Karrer, Stoll, and Stevens²³ state that they obtained the value of 1150 instead of 1319 in the molecular weight calculation. The viscosity measurements show likewise that a degradation of the molecules has taken place, for the viscosity of a hydrocarbon of a molecular weight of 1319 would have to be greater than that found.

TABLE IV
TETRALIN SOLUTIONS AT 20°

Substance	Molecular Weight	Chain Equivalent Weight	Number of Chain Atoms	η_r	η_{sp} in a 7% Solution	η_{sp} Found in Chain-Equivalent Solution	η_{sp} Calculated in Chain-Equivalent Solution ($0.85 \times M$)	η_{sp} Found in 1.4% Solution	η_{sp} Calculated in 1.4% Solution ($1.2 \times 10^{-3} \times \eta$)
Perhydroqualene $C_{10}H_{16}$	422	17.5	24	1.147	0.147	0.0368	0.036	0.029	0.029
				(in 7% soln.)		(in 1.75% soln.)			
Dibixane $C_{16}H_{24}$	647	17.0	38	1.107	0.245	0.0594	0.055	0.049	0.046
				(in 3.1% soln.)		(in 1.70% soln.)			
Tetrabixane $C_{24}H_{36}$	Theoret. 1319	17.4	76	0.112	...	0.091
Tetrabixane $C_{24}H_{36}$	Found by Karrer 1150	17.4	66	0.098	...	0.079
Tetrabixane $C_{24}H_{36}$	Found Table III 960	17.4	55	0.082	...	0.066
Tetrabixane $C_{24}H_{36}$	Calculated from the viscosity 1070	17.4	Calculated 61	1.117	0.365	0.091	...	0.073	...
				(in 2.2% soln.)		(in 1.74% soln.)			

TABLE V
BENZENE SOLUTIONS AT 20°

Substance	Molecular Weight	Chain Equiva- lent Weight	Number of Chain Carbon Atoms	η_r	η_{sp} (7% Solution)	η_{sp} Found in Chain- Equivalent Solution	η_{sp} Calculated in Chain- Equivalent Solution (1.0 X 10 ⁻¹ X M)	η_{sp} Found in 1.4% Solution	η_{sp} Calculated in 1.4% Solution (1.4 X 10 ⁻¹ X M)
Tetramethylhexa- decane C ₁₈ H ₃₈	282	17.6	16	1.133 (8.3% soln.)	0.112	0.0282 (1.76% soln.)	0.0282	0.022	0.022
Hexahydrosqua- lene C ₁₀ H ₁₈	422	17.6	24	1.075 (3.1% soln.)	0.167	0.0420 (1.75% soln.)	0.0422	0.033	0.034
Dibixane C ₁₆ H ₃₄	674	17.0	38	1.119 (3.0% soln.)	0.277	0.0673 (1.7% soln.)	0.0647	0.055	0.053
Tetrabixane C ₁₆ H ₃₀	Theoret. 1319	17.4	76	0.132	...	0.106
Tetrabixane C ₁₆ H ₃₀	Found by Karrer 1150		66	0.115	...	0.062
Tetrabixane C ₁₆ H ₃₈	Found Table III	17.4	55	0.096	...	0.077
Tetrabixane C ₁₆ H ₄₀	Calculated from viscosity 984	..	Calculated 56	1.265 (4.7% soln.)	0.396	0.0984 (1.74% soln.)	0.079	...

From viscosity measurements the molecular weight can also be calculated according to the above equation, if the chain-equivalent weight of a hydrocarbon is known. For tetrabixane calculations show a chain-equivalent weight of

$$\frac{1319}{76} = 17.4$$

It can be assumed that this chain-equivalent weight also remains unchanged in the somewhat degraded tetrabixane. In that case calculations of the viscosity show a molecular weight of 1070. In a further determination of the molecular weight by the method of Rast in camphor the following values were obtained.

A simple relation exists between the specific viscosity and the length of the chain of the fiber molecules, which can be expressed in the following way: *Solutions of hydrocarbons of equal viscosity and of equal concentration contain fiber molecules of the same length of chain.* This relation makes it possible to calculate the viscosity of dilute solutions of hydrocarbons of known length of chain, and conversely to calculate from viscosity measurements the unknown chain length and therefore the molecular weight of hydrocarbons of unknown chain length, in case the chain-equivalent weight is known. For 1.4 per cent solutions of hydrocarbons in tetralin the following relation is applicable:

$$\eta_{sp}(1.4\%) = K_{equiv.} \times 14 \times n = 0.85 \times 10^{-4} \times 14 \times n = 1.2 \times 10^{-3} \times n$$

where n is the length of chain of the hydrocarbon. The specific viscosity of 1.4 per cent solutions of hexahydrosqualene and of dibixane calculated to this formula agrees approximately with that found by viscosity measurements. On the contrary, with tetrabixane, too high a value is obtained if a carbon chain of 76 carbon atoms is assumed. The viscosity measurements indicate a carbon chain of about 56 carbon atoms. The molecular weight of a hydrocarbon is equal to the product of the number of the members of the chain and the chain-equivalent weight. Accordingly for tetrabixane the value of $56 \times 17.4 = 985$ is obtained, or a value which agrees approximately with that calculated by the first method and by cryoscopic determinations.

In the case of this hydrocarbon, therefore, the relation between viscosity and molecular weight found with the different homologous polymeric substances²⁵ was confirmed. These relations, therefore, make possible the calculation of the molecular weight of hydorrubber, with the result that the highest molecular product has a molecular weight of about 50,000.

These valuable hydrocarbons, dibixane and tetrabixane, which furnish an important confirmation of our concept of the constitution of hydorrubber, were placed at our disposal through the kind assistance of P. Karrer, to whom we take this opportunity of expressing our thanks.

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- ⁴ *Ann.*, **435**, 303 (1924).
- ⁵ *Helvetica chim. acta*, **13**, 1355 (1930).
- ⁶ Thesis by Leupold soon to be published.
- ⁷ *Helvetica chim. acta*, **14**, 1194 (1931).
- ⁸ Karrer, *et al.*, *Ibid.*, **13**, 1084 (1930); **14**, 435 (1931).
- ⁹ Tsujimoto, *Chem. Zentr.*, **1918**, I, 639; Heilbron, Hilditch, and Kamm, *J. Chem. Soc.*, **1926**, II, 3131. Heilbron has most kindly furnished the squalene used by us in these investigations.
- ¹⁰ Fischer and Löwenberg, *Ann.*, **485**, 204 (1929). Fischer furnished a sample for the viscosity measurements, and we wish to thank him at this time.

- ¹¹ Staudinger and Fritsch, *Helvetica chim. acta*, **5**, 785 (1922); Staudinger, *Ber.*, **57**, 1203 (1924); Staudinger and Schaal, *Helvetica chim. acta*, **13**, 1355 (1930).
- ¹² *Ann.*, **438**, 309 (1924).
- ¹³ *Helvetica chim. acta*, **14**, 1194 (1931).
- ¹⁴ Meyer, *Z. angew. Chemie*, **41**, 943, Section XV (1928).
- ¹⁵ Fischer and Tropsch, *Ber.*, **60**, 1330 (1927); Staudinger, Brunner, and Feisst, *Helvetica chim. acta*, **13**, 818 (1930).
- ¹⁶ The polymer methylene, arising from catalytic decomposition of diazomethane, is perhaps a high polymeric paraffin. Bamberger, *Ber.*, **33**, 956, Note 3 (1900); Meerwein and Burneleit, *Ibid.*, **61**, 1843, Note 9 (1928).
- ¹⁷ Dunkel, *Z. physikal. Chemie (A)*, **138**, 42 (1928).
- ¹⁸ Meyer, *Z. angew. Chemie*, **41**, 933 (1928).
- ¹⁹ Staudinger and Nodzu, *Ber.*, **63**, 721 (1930); Staudinger and Ochiai, *Z. physikal. Chemie (A)*, **158**, 35 (1931).
- ²⁰ Staudinger and Heuer, *Ber.*, **63**, 222 (1930); Staudinger, *Kolloid-Z.*, **51**, 71 (1930).
- ²¹ Staudinger and Nodzu, *Helvetica chim. acta*, **13**, 1352 (1930).
- ²² Staudinger, *Ibid.*, **15**, 213 (1932); High polymeric compounds, Part 60, *Berichte*, Feb. 1932.
- ²³ *Helvetica chim. acta*, **14**, 1194 (1931).
- ²⁴ Only a very small quantity of the material was available for these molecular weight determinations.
- ²⁵ Staudinger and Heuer, *Ber.*, **63**, 222 (1930); Staudinger, *Z. physikal. Chemie (A)*, **153**, 391 (1931); High polymeric compounds, Part 60, *Berichte*, Feb. 1932.

An Inorganic Rubber

Paul Renaud

Several chloronitrides of phosphorus, corresponding to the formula $(\text{PNCl}_2)_n$, are known and some definite products have been isolated where n is 3, 4, 5, 6, and 7. When heated around 270° in sealed tubes, they give gums similar to rubber (see Schenck and Römer, *Ber.*, **57**, 1343 (1924)). On the basis that the principal factors in this polymerization are the temperature and the time of heating, the polymerization was studied by starting with a trimer which had been washed, twice distilled, and dried a long time, since traces of water modify the polymerization greatly. In this way a large number of forms of variable melting points were obtained, and of which the average molecular weights increase with the length of time and the temperature of heating.

Some of the gummy forms are infusible and insoluble, and it was not possible to determine their molecular weights. Particular attention was paid to a study of these forms. To the touch, they resemble rubber. Some are very pliable and when stretched show a considerable resilient force. At ordinary temperature they adhere strongly to the walls of the glass tubes, whereas at low temperatures they are easily removed.

Some have the appearance of a transparent but immobile liquid containing immutable bubbles; others have the appearance of a mass of crystals. If one of these latter forms is heated slowly, it loses its crystalline appearance and becomes a transparent liquid without mobility. The gum is slightly more pliable to the touch. Thermal analysis shows that the heat liberated in this apparent fusion is not negligible. When heated to a higher temperature, these products decompose without fusion.

It is probable that these optical melting points can be represented by curves similar to those of true fusion, *i. e.*, similar to the curves of mixtures. It has not been possible to determine these curves because many of the forms show superfusion to a high degree, and agitation favorable to arrangement of the molecules is impossible.

M. Mathieu has very kindly examined these gums by x-rays. Those which are optically liquid give a diagram of liquids. Optically solid products give a diagram of crystals with a continuous ground, while the crystals of the trimer give a diagram of crystals.

When cooled in liquid air, the gums assume the appearance of glass. When struck with a stirring rod the sound is dull, but after cooling it is sharp and clear; in the cold the substance, originally pliable, becomes hard and brittle. The change takes place within a narrow range of temperature which may be considered a "point of mechanical transformation," around -47° , which is within a few degrees for all these forms. Moreover, at the same temperature two gums always give the same sound, no matter what the temperature may be. There are accordingly thermo-mechanical properties common to all these gums.

These gums swell in benzine without dissolving. When stirred for a long time in this liquid they leave an insoluble residue and the solutions obtained deposit crystals upon evaporation. When heated *in vacuo* around 500° , a product distills which is sometimes crystalline and sometimes liquid, composed of polymers of low molecular weight. The proportion of crystals obtained is the same in both cases.

A black insoluble residue is left. The melting point of the crystals recovered and the optical transformation point of the gum are within a few degrees of the same temperature. If the gum is heated *in vacuo* to a temperature lower than 400° it does not distil at all, although the boiling point of the melted crystals is below 400°.

When benzine is added to these irreversible gels, a reversible gel is obtained. On the other hand, they do not swell in water.

Conclusions

The hypotheses generally accepted for the structure of gels explain these phenomena in detail.

The trimer, polymerized by heating, gives rise to chains of different sizes, which are able to unite and form a network. The latter contains in its meshes the trimer which has not reacted, and also polymers of low molecular weight. According to whether the latter form a liquid or solid mixture, the gum is optically liquid or solid.

At low temperature, the network itself assumes a rigidity which it communicates to the entire mass. The thermo-mechanical properties show that this is true of all the gums. The presence of the network has little influence on the fusion of the intercellular product, whereas its influence on vaporization is great; in fact, the volume is as little affected by fusion as it is greatly changed by vaporization. It must therefore be the case that rupture of the meshes by pressure is more rapid than their formation by polymerization. The influence of benzine and of water, one of which dissolves the intercellular products and the other does not, shows the influence of osmotic pressure, to which Duclaux (see *Bull. soc. chim.*, 33, 36 (1923)) has called attention.

The Oxidation of Rubber Gutta-Percha and Balata with Hydrogen Peroxide

John A. Mair and John Todd

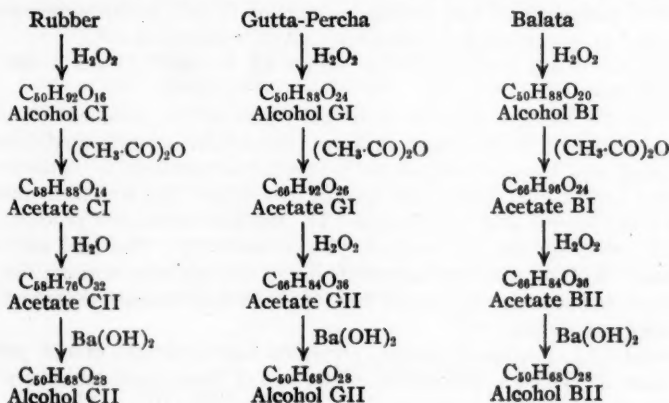
UNIVERSITY OF GLASGOW, SCOTLAND

The behavior of rubber toward hydrogen peroxide was studied first by Boswell, McLaughlin, and Parker (*Trans. Roy. Soc. Can.*, 16, 27 (1922)) and more recently by Robertson and Mair (*J. Soc. Chem. Ind.*, 46, 41T (1927)).

The earlier workers, using a solution of rubber in carbon tetrachloride, isolated a compound, $C_{30}H_{48}O$, which they found to absorb atmospheric oxygen and yield another compound, $C_{26}H_{40}O_2$. The later workers adopted a modification of the usual method of hydrogen peroxide oxidation of terpene hydrocarbons and employed a chloroform solution of rubber, to which glacial acetic acid was added. They obtained a product, alcoholic in character, of the empirical formula $C_{50}H_{82}O_{16}$. The present work was commenced with the object of extending the latter work to include gutta-percha and balata. Certain changes were introduced and new avenues of investigation opened up, and it was thought desirable to extend the scope of the work to include rubber so that each of the three substances, rubber, gutta-percha, and balata, and corresponding derivatives of them, might be submitted to as nearly as possible identical reaction conditions.

Since all the products were non-crystalline solids which decomposed on distillation, even under reduced pressure, it was almost impossible to obtain a complete separation from resinous materials once these were formed. Therefore, every effort was made to reduce to a minimum the risk of the formation of such undesirable by-products. Polymerization took place very readily, even when solutions of the products were warmed to temperatures above 50° , and all operations were carried out at temperatures not exceeding 40° to avoid this difficulty. There was little difference in the behavior of the various products toward solvents, and this increased the difficulty of their purification.

The main results of the work have been embodied in the accompanying diagram.



In order to obtain a general idea of the relationship existing throughout the whole series, the empirical formulas which are suggested for the various products have been reduced to a common unit, C_{50} , the lowest one consistent with the analyses of the semicarbazones and acid salts to be described later. The discrepancies noticeable in some cases between actual and calculated analyses are only to be expected, because no criterion is available to guarantee the absolute purity of any of the products.

Rubber

Rubber in chloroform solution, to which glacial acetic acid had been added, was oxidized with 100-vol. hydrogen peroxide and yielded a colorless amorphous compound, alcoholic in character, approximating, after reduction to a C_{50} basis, $C_{50}H_{92}O_{16}$. It was still unsaturated to bromine and to dilute alkaline permanganate, did not possess acidic or reducing properties, and was thought to be an alcohol corresponding to the usual products of hydrogen peroxide oxidation in the terpene series. Estimation by the method of Tschugaev and Zerewitinov (*Ber.*, 35, 3912 (1902); 40, 2023 (1907)) indicated that all the oxygen was present as hydroxyl. The compound was therefore $C_{50}H_{76}(OH)_{16}$ and was probably produced from rubber by simple addition of hydroxyl groups to the unsaturated linkages of the parent molecule. Accurate determination of its molecular weight by the cryoscopic method was impossible and values obtained by the Rast method, using camphor or menthol as solvent, varied considerably and were of no use in fixing the actual molecular weight: camphor gave values in the neighborhood of 1000, and with menthol as solvent values from 600–1000, varying with concentration, were obtained.

The unsaturation as determined by measuring the absorption of bromine by the method of Gladstone and Hibbert (*J. Chem. Soc.*, 53, 679 (1888)) was greater than that required for a compound of the type C_nH_{2n} . Possibly this was due to some oxidizing action of the bromine. No characteristic derivative of this alcohol could be obtained, owing to the impossibility of separating the main product in each case from resinous by-products.

By oxidation of alcohol CI with chromic acid, a substance, aldehyde CI, was obtained having pronounced aldehydic properties. The semicarbazone obtained from it gave the analytical values required for the formula $C_{50}H_{88}O_{16}(CN_2H_3)_2$ —indicating the presence in the aldehyde of two CHO groups per C_{50} and, consequently, the presence, in alcohol CI, of two CH_2OH groups per C_{50} .

Further oxidation of aldehyde CI by means of dilute nitric acid yielded an acid, the silver salt of which had a silver content of 17.78% in fair agreement with the calculated silver content for $C_{48}H_{86}O_{14}(CO_2Ag)_2$, namely, 18.15%.

From these facts the formula for alcohol CI on the C_{50} basis would be $C_{48}H_{72}(OH)_{14}(CH_2OH)_2$.

Alcohol CI was treated with acetic anhydride in the presence of anhydrous sodium acetate, and it was found that the product did not give analytical results in agreement with those calculated for the acetate of alcohol CI. This new product, acetate CI, was hydrolyzed with baryta to alcohol CIA, which, in turn, was oxidized with chromic acid to aldehyde CII; the last-mentioned product, on further oxidation with atmospheric oxygen, yielded acid CII. The lead salt of acid CII contained 18.9% of lead and indicated that, if the salt were normal, the acid would be dibasic and of molecular weight 890. It is on this evidence that the C_{50} basis for the series was chosen.

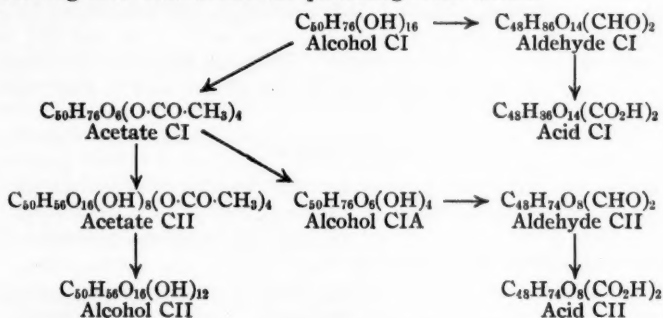
Alcohol CIA, mentioned above, possessed four hydroxyl groups per $C_{50}H_{80}O_{10}$ and, since it yielded a dialdehyde (CII), two of these must have been present as primary alcoholic groups, giving $C_{48}H_{72}O_8(OH)_2(CH_2OH)_2$. Aldehyde CII would

then be $C_{48}H_{72}O_6(OH)_2(CHO)_2$, yielding the semicarbazone $C_{50}H_{76}O_{10}(CN_3H_3)_2$, and acid CII would be $C_{48}H_{74}O_8(CO_2H)_2$, giving the lead salt $C_{48}H_{74}O_8(CO_2)_2Pb$.

Since alcohol CIA, $C_{50}H_{76}O_6(OH)_4$, was derived, by hydrolysis, from acetate CI, the latter compound must have been $C_{50}H_{76}O_6(O-CO-CH_3)_4$. Now, acetate CI was derived from alcohol CI, $C_{50}H_{76}(OH)_{16}$, so it would appear that, under the influence of the acetic anhydride, loss of the elements of water had accompanied acetylation of several of the hydroxyl groups.

Acetate CI was still unsaturated and, on further treatment with 100 vol. hydrogen peroxide, yielded acetate CII, $C_{50}H_{76}O_{32}$, containing free hydroxyl groups in addition to the acetoxy-groups of the original acetate. Alcohol CII, $C_{50}H_{56}O_{16}(OH)_{12}$, was produced by the action of aqueous baryta on acetate CII, which was then assigned the formula $C_{50}H_{56}O_{16}(OH)_8(O-CO-CH_3)_4$. Acetate CII and alcohol CII were both saturated to bromine and therefore represent the final stage of the oxidation process.

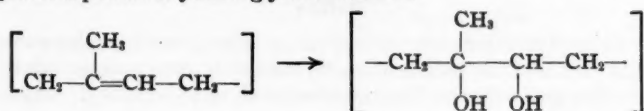
The following table summarizes the preceding observations:



It is suggested that the changes recorded above have been brought about by the addition of hydroxyl groups to double bonds under the influence of hydrogen peroxide, and subsequent removal of the elements of water through the action of acetic anhydride. There is no evidence of extensive degradation of the hydrocarbon molecule involving loss of carbon, the proportion of acidic products formed during the oxidations being very small. In this respect the action of hydrogen peroxide on rubber differs materially from that of neutral or alkaline potassium permanganate. In the latter case there is evidence of extensive degradation, as shown by the formation of substantial amounts of levulinic and oxalic acids. In addition, the proportion of carbon liberated as carbon dioxide corresponds approximately to the oxidation of only 0.5% of the total carbon of the hydrocarbon.

No attempt has been made to distinguish between the cyclic and open-chain formulas in interpreting the experimental results. The C_nH_{2n} form has been used throughout, since, on the whole, it agrees best with the values obtained for the unsaturation of the various products. The C_{50} basis on which the empirical formulas have been calculated represents the minimum unit within which all the oxidation products can be included, and permits of their arrangement according to a definite scheme. It is of course obvious that a great number of alternative empirical formulas could be assigned to any one product in dealing with such large molecular weights.

Taking the accepted unit of the rubber molecule, oxidation with hydrogen peroxide might be expected to yield a glycol as follows:



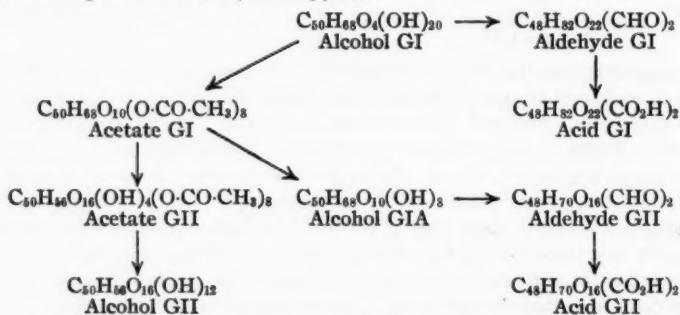
Removal of the elements of water might take place in several ways. If two adjacent hydroxyl groups were involved, the result would be an outside ether ring, whereas, if two hydroxyls on opposite sides of the molecule were concerned, an inner ether ring would be formed. Finally, elimination of water between a hydroxyl group and the hydrogen of an adjacent methylene group would give rise to a new double bond. Since the observed loss of water does not lead to an increase in unsaturation, as would occur in this case, the double linkages thus formed must rearrange to give a ring system inside the molecule. Oxide formation seems most probable, since the methylene groups are themselves apparently involved in a further oxidation.

Between acetate CI and acetate CII there is a considerable replacement of hydrogen by oxygen. This is evident from a consideration of the corresponding alcohols.

Alcohol CIA has the empirical formula $C_{50}H_{76}O_6(OH)_4$ and has an unsaturation equal to four double bonds. Addition of hydrogen peroxide (to its acetyl derivative) should give a saturated alcohol $C_{50}H_{76}O_6(OH)_{12}$, and this should be identical with alcohol CII, the end-product of the oxidation series. Alcohol CII, however, has the empirical formula $C_{50}H_{56}O_{16}(OH)_{12}$. There has therefore been replacement of hydrogen by oxygen to the extent of twenty atoms, and in this reaction the methylene groups must be involved.

Gutta-Percha

Gutta-percha was treated in a manner similar to that described for rubber and under as nearly as possible identical reaction conditions. The results are incorporated in the following table, in which all the formulas have been reduced to the same basis as that adopted for rubber, namely, C_{50} .

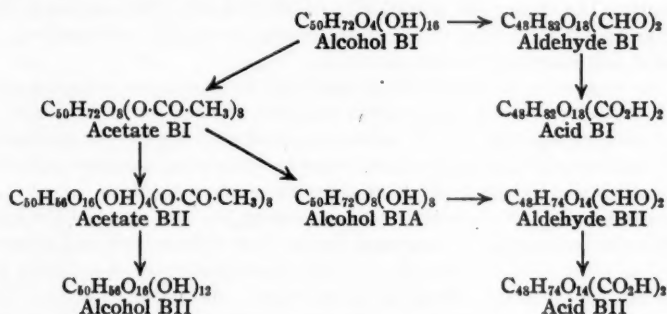


The products were very similar to those obtained from rubber. They also seem to have been produced by a series of reactions involving the addition of hydroxyl groups, followed by the removal of the elements of water. The gutta-percha hydrocarbon, however, seems to be more readily attacked by hydrogen peroxide than is rubber, the larger proportion of oxygen in the primary product, alcohol GI, being probably a result of this. It would also appear that the replacement of hydrogen by oxygen, already noted in the case of rubber, has occurred in the first stage of the gutta-percha oxidation, since the alcohol formed by addition of hydroxyl to the hydrocarbon, and corresponding in unsaturation to alcohol GI, should be $C_{50}H_{80}(OH)_{16}$ instead of $C_{50}H_{68}O_4(OH)_{20}$.

Balata

A similar series of reactions was carried out on balata, and a similar series of products isolated. Each of the balata products seemed to bear a closer relationship to the corresponding gutta-percha products than to those from rubber. Again alcohol

BI gave an analysis indicating an initial replacement of hydrogen by oxygen as in alcohol GI. The results are summarized below.



It will be seen that the end-product, alcohol II, in each of the three series has been assigned the same empirical formula, the analytical results being sufficiently in agreement to justify this conclusion. In the absence of other data it cannot be said that these alcohols are identical, but a close similarity in structure seems probable.

The preceding results show that it is possible to obtain an oxidation series of corresponding terms for the three hydrocarbons, rubber, gutta-percha, and balata. The physical properties of the products indicate that the oxidation is accompanied by more or less extensive depolymerization.

Rubber, gutta-percha, and balata may be regarded as condensation products of isoprene, an undetermined number of isoprene molecules condensing to give a cyclic or open-chain hydrocarbon with approximately one-half of the initial unsaturation of the isoprene molecules involved. Further aggregation of the condensed isoprene molecules takes place through partial valences to give the rubber, gutta-percha, or balata complex. These complexes can be partly broken down by suitable solvents, presumably as a result of solvation. On this basis the treatment of rubber, etc., with oxidizing agents should cause depolymerization by saturation of the available double bonds, with consequent disappearance of the secondary valencies. Should the complex aggregate be of different dimensions in the three hydrocarbons, oxidation would be expected to give different intermediate products owing to the varying number of partial valences involved in each case. The preceding results seem to justify this view, the close resemblance between the final oxidation products being probably due to complete saturation of the double bonds of the fundamental unit produced by the initial isoprene condensation. This view of the mechanism of oxidation is borne out by the observation that the process must be carried out in stages, it being found impossible to secure complete saturation of the hydrocarbons by a single oxidation process. It should be noted, as regards the intermediate oxidation products, that although the end-point of the first stage of oxidation of the hydrocarbons was an arbitrary one, it was reached in each case by an identical procedure and provides a reasonable basis for comparison.

If the suggestion put forward that the later stages of oxidation involve not only addition of hydroxyl to the double bonds of $\left[\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array} \right]$ but also oxidation of the methylene groups is correct, the direct addition of hydroxyl to rubber in the first stage of the oxidation, without replacement of hydrogen by oxygen as occurs in BI and GI, and the occurrence of the latter action in the second

stage of the rubber oxidation, would indicate that the reaction has further to go with rubber to reach the point of saturation represented by the fully oxidized fundamental unit. The molecular complexity of the rubber hydrocarbon is therefore apparently greater than that of the gutta-percha or balata hydrocarbon, the last two being of a similar order of complexity.

From the experimental results it appears that the minimum complex unit of all three hydrocarbons contains ten isoprene residues, or some multiple of this number. From the general behavior of the oxidation products, themselves undoubtedly of high molecular weight, it seems probable that the minimum complex unit of the hydrocarbons contains substantially more than ten isoprene residues.

The proportion of carbon dioxide evolved during the first stage of the oxidations varies with the hydrocarbon concerned, being least with rubber and greatest with balata. Assuming that its formation in each case is the result of a similar reaction, the minimum complex unit of rubber is the largest, consisting of at least forty isoprene residues. This supports the conclusion, drawn from the results in the oxidation series, as to the relative complexity of the three hydrocarbons.

Experimental

Purification of Raw Materials.—The rubber, prepared from crepe which was in the form of thin sheets of a pale yellow color, was purified by Harries' standard method, consisting of extraction with acetone in a Soxhlet apparatus, followed by dissolution of the hydrocarbon in benzene, and reprecipitation of the rubber from the filtered solution by means of alcohol.

The gutta-percha and balata hydrocarbons were purified by a different method. To 20–25 g. of the crude shredded material were added 400–500 cc. of boiling petroleum (b. p. 60–80°) and the mixture was kept at 40° until the insoluble material had settled. On cooling, the hydrocarbon settled out from the solution and was separated easily from the residue, insoluble in hot or cold petroleum, and from the resins, soluble even in the cold solvent. The precipitated hydrocarbon was submitted to several similar treatments, fresh petroleum being used each time and kaolin added, when necessary, to facilitate settling of the suspended matter. The final products were colorless solids of a leather-like consistency, transparent in hot alcohol, and readily oxidized on exposure to the air, becoming brown and friable.

Action of 100 Volumes of Hydrogen Peroxide on the Hydrocarbons.—The method adopted for the oxidation was that used by Robertson and Mair (*J. Soc. Chem. Ind.*, 46, 417 (1927)), a solution of the hydrocarbon in chloroform and glacial acetic acid being treated with 100 volumes of hydrogen peroxide. In the earlier oxidations the proportions of reagents employed by the earlier workers were used, but products which varied a good deal on analysis were obtained.

The final reaction mixture was: 25 g. of the hydrocarbon, 350 cc. of chloroform, 250 cc. of glacial acetic acid, and 55 cc. of 100-vol. hydrogen peroxide. The hydrocarbon was dissolved in the chloroform, and the hydrogen peroxide added with shaking. Precipitation of part of the hydrocarbon occurred. The mixture was kept at 40° until homogeneous. The products were extracted with chloroform, the combined extracts washed with dilute sodium carbonate solution and water and dried over anhydrous sodium sulfate, and the chloroform removed under reduced pressure below 40°. The residue, a pale yellow glassy solid, was freed from any unattacked hydrocarbon by solution in alcohol, decantation from insoluble hydrocarbon, and removal of the solvent under reduced pressure. The product was obtained finally in a workable form by slow dropping of an acetone solution into a mechanically stirred solution of sodium chloride.

In some cases the hydrogen peroxide oxidation followed an irregular course, giving products of abnormal composition, due apparently to partial polymerization. Measurements of the unsaturation were adopted as a guide to the course of the reaction, products giving abnormal values being rejected. The products studied were those giving the maximum observed unsaturation. Those having lower values were assumed to have undergone partial cyclization.

In the initial stages of the reaction carbon dioxide was evolved in varying proportions, the maximum yield observed in the case of rubber being equivalent to the oxidation of 0.5% of the carbon of the rubber, corresponding to the oxidation of one carbon atom per C_{200} . In the oxidation of gutta-percha and balata the largest yields of carbon dioxide measured were equivalent to 1.0% and 1.4%, respectively, of the carbon of the parent substances, corresponding to the oxidation of one carbon atom per C_{100} and C_{70} , respectively.

The yields of the oxidation products being almost quantitative, no special effort was made to extract any acid products from the reaction mixture, containing, as it did, such a large proportion of acetic acid.

The Oxidation Products.—The three products were odorless, colorless, amorphous solids, insoluble in water, light petroleum, carbon tetrachloride, and carbon disulfide, sparingly soluble in benzene and ether, and very soluble in methyl and ethyl alcohol, acetone, chloroform, ethyl acetate, acetic acid, and pyridine. They were neutral in character and did not possess reducing properties, but were unsaturated to bromine and to dilute alkaline permanganate solution. On distillation *in vacuo* they decomposed, giving dark oily distillates.

Ultimate analysis of the oxidation products gave the following results:

Rubber. Found: C, 62.6, 62.9; H, 9.9, 9.7 ($C_{50}H_{92}O_{16}$ requires C, 63.3; H, 9.7%).

Gutta-Percha. Found: C, 55.6, 55.3; H, 8.2, 8.2 ($C_{50}H_{88}O_{24}$ requires C, 55.9; H, 8.2%).

Balata. Found: C, 57.6, 57.6; H, 8.6, 8.5 ($C_{50}H_{88}O_{20}$ requires C, 59.5; H, 8.7%).

The hydroxyl contents of the alcohols and their unsaturations, determined by the methods mentioned on page 588, were as follows (the unsaturations are expressed in g. of bromine per 100 g. of oxidation product).

Oxidation Product	Hydroxyl Content		Unsaturation	
	Found, %	Calc., %	Found, %	Calc., %
Rubber	29.6, 29.0	28.7	85.0, 85.7	67.3
Gutta-Percha	32.2, 32.0	31.7	44.9, 44.8	29.8
Balata	25.8, 25.7	27.0	47.0, 46.8	31.7

The considerable discrepancy in each case between the unsaturation found and that calculated from the empirical formula corresponds actually to almost exactly one additional double bond per C_{50} . Whether this irregularity is due to oxidation by the bromine or to rupture of the ring system cannot be decided, since none of the brominated oxidation products was sufficiently stable to permit of its isolation and analysis.

Action of Chromic Acid on the Alcohols.—The above alcohols, failing to yield a satisfactory derivative, were treated with chromium trioxide in glacial acetic acid solution. The reaction mixtures used were as follows:

Rubber		Gutta-Percha and Balata	
A	{ 10 g. alcohol CI 80 cc. glacial acetic acid	A	{ 10 g. alcohol GI or BI 80 cc. glacial acetic acid
B	{ 1.4 g. chromium trioxide 40 cc. glacial acetic acid	B	{ 1.2 g. chromium trioxide 40 cc. glacial acetic acid

Solution A, to which a few drops of water were added, was cooled in a freezing mixture and mechanically stirred, and solution B, also cooled, was added drop by drop. Rapid mixing of the reagents caused the formation of resinous acids. The reaction was completed at room temperature overnight, the mixture was then thrown into water, and the acid just neutralized with sodium carbonate. A white solid which separated was extracted repeatedly with ether, the combined extracts being washed with water and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a colorless glassy solid, which was taken up again in acetone and reprecipitated with sodium chloride solution.

The three products in appearance were practically identical. They were colorless amorphous solids, insoluble in water, benzene, and light petroleum, sparingly soluble in ether, and very soluble in methyl and ethyl alcohols, acetone, chloroform, and acetic acid. They reacted with ammoniacal silver oxide, Fehling solution, and Schiff reagent. The sodium bisulfite compound of each was obtained only after several weeks' exposure to the reagent, the semicarbazone after about a week. In each case it was a colorless, odorless, amorphous solid, insoluble in water, benzene, toluene, ether, and carbon tetrachloride, sparingly soluble in chloroform, and very soluble in methyl and ethyl alcohols, acetone, and in ethyl acetate. Found for the semicarbazones: (rubber) C, 58.1, 58.0; H, 8.9, 8.8; N, 7.8, 7.8 ($C_{42}H_{94}O_{16}N_6$ requires C, 59.0; H, 8.9; N, 7.9%); (gutta-percha) C, 52.6, 52.1; H, 7.6, 7.7; N, 7.1, 7.0 ($C_{42}H_{90}O_{14}N_6$ requires C, 52.8; H, 7.6; N, 7.1%); (balata) C, 56.0, 55.8; H, 7.8, 7.9; N, 7.5, 7.4 ($C_{42}H_{90}O_{20}N_6$ requires C, 55.8; H, 7.9; N, 7.5%).

Action of Nitric Acid on the Aldehydes.—The aldehyde was left in contact with dilute nitric acid (5 cc., d. 1.42, in 15 cc. of water) for 4 days at the ordinary temperature. The acid product was extracted by means of ether from the reddish solution.

The three products were fawn-colored granular solids, insoluble in water, benzene, toluene, and light petroleum, soluble in ether, methyl and ethyl alcohols, acetone, and in dilute solutions of sodium carbonate and caustic alkali. They did not contain nitrogen, but when a more concentrated acid was used, the products were dark brown and contained nitrogen. When the reaction mixture was heated, a resinous mass, containing nitrogen and acidic, was obtained.

Only the silver salts were obtained and these decomposed readily. Found: (rubber) Ag, 17.86, 17.68 [$C_{43}H_{86}O_{14}(CO_2Ag)_2$ requires Ag, 18.15%]; (gutta-percha) Ag, 16.32, 16.27 [$C_{43}H_{82}O_{22}(CO_2Ag)_2$ requires Ag, 16.44%]; (balata) Ag, 17.02, 16.94 [$C_{45}H_{82}O_{18}(CO_2Ag)_2$ requires Ag, 17.28%].

Action of Acetic Anhydride upon the Alcohols.—Each of the alcohols was treated with acetic anhydride in presence of fused sodium acetate for 3 hours at 30°. When the reaction mixture was poured into water, the product was precipitated as a yellowish paste, which was taken up in acetone and reprecipitated several times by means of sodium chloride solution.

The products were colorless, odorless, amorphous solids, insoluble in water, benzene, toluene, carbon tetrachloride and light petroleum, and soluble in ether, methyl, and ethyl alcohols, chloroform, acetone, ethyl acetate, and pyridine. Found: (rubber) C, 68.5, 68.7; H, 8.7, 8.4 ($C_{53}H_{88}O_{14}$ requires C, 69.0; H, 8.7%); (gutta-percha) C, 61.4, 60.9; H, 7.0, 7.1 ($C_{66}H_{92}O_{26}$ requires C, 60.9; H, 7.1%); (balata) C, 61.8, 62.0; H, 7.3, 7.4 ($C_{66}H_{96}O_{24}$ requires C, 62.2; H, 7.5%).

The acetyl content of each was determined by the Perkin method, and the unsaturation by the usual method:

Acetate	Acetyl Content		Unsaturation	
	Found, %	Calc., %	Found, %	Calc., %
Rubber	19.6, 18.9	17.1	64.8, 64.7	63.5
Gutta-Percha	25.9, 25.3	26.4	24.7, 24.8	24.6
Balata	26.4, 26.3	27.0	25.4, 25.3	25.3

Hydrolysis of the Acetates.—This was effected by treatment with aqueous baryta for several hours at 30° and was possible only on a small scale, as, when larger quantities were used, the hydrolysis was difficult to control. The resulting alcohols were purified by repeated fractional precipitation from ethyl acetate solution by means of ether, in which solvent the alcohols were less soluble than the corresponding acetates. The purest specimens were colorless. Found: (rubber) C, 70.8, 71.2; H, 9.6, 9.4 ($C_{50}H_{80}O_{10}$ requires C, 71.4; H, 9.5%); (gutta-percha) C, 60.8, 61.3; H, 7.8, 7.6 ($C_{50}H_{74}O_{18}$ requires C, 62.2; H, 7.9%); (balata) C, 63.5, 64.2; H, 8.4, 8.4 ($C_{50}H_{80}O_{18}$ requires C, 64.1; H, 8.5%).

Alcohol	Hydroxyl Content		Unsaturation	
	Found, %	Calc., %	Found, %	Calc., %
Rubber	8.3, 8.6	8.1	76.5, 76.8	76.2
Gutta-Percha	13.4, 13.0	14.1	31.3, 31.5	33.2
Balata	14.2, 14.3	14.5	33.6, 33.5	34.2

Oxidation of the Alcohols.—Chromium trioxide in glacial acetic acid solution was used, as before, to oxidize the new alcohols. The three products were colorless amorphous solids, insoluble in water, benzene, and light petroleum, sparingly soluble in ether, and very soluble in alcohol, acetone, chloroform, and acetic acid. They all gave the usual tests for an aldehyde group. From alcoholic extracts, semicarbazones were prepared in the usual way. These were amorphous solids, colorless and without odor. They were insoluble in water, ether, and the hydrocarbon solvents and were very soluble in alcohol and acetone. Found: (rubber) C, 64.8, 65.0; H, 8.7, 8.7; N (Kjeldahl), 8.8, 8.8 ($C_{52}H_{82}O_{10}N_8$ requires C, 65.7; H, 8.6; N, 8.8%); (gutta-percha) C, 58.4, 58.6; H, 7.1, 7.1; N, 7.7, 7.7 ($C_{52}H_{78}O_{18}N_8$ requires C, 58.1; H, 7.3; N, 7.8%); (balata) C, 60.2, 60.0; H, 7.7, 7.7; N, 8.0, 7.9 ($C_{52}H_{82}O_{18}N_8$ requires C, 59.6; H, 7.8; N, 8.0%).

Oxidation of the Aldehydes.—The products resulting from the treatment of the above aldehydes with dilute nitric acid were not acidic and contained a fair proportion of nitrogen. By drawing a current of air through an alcoholic solution of the aldehyde at 40°, an acid product was obtained. Removal of the solvent from an ethereal extract of the reddish solution left a reddish syrup which was to a large extent soluble in dilute sodium carbonate solution. A brown gelatinous precipitate was formed on acidification of the alkaline solution. The acid was taken up several times in dilute aqueous sodium carbonate, the solution filtered, and the product reprecipitated by addition of acid. The filtered, washed, and dried product was a brown, friable solid.

The three acids were insoluble in water, benzene, toluene, and light petroleum, soluble in ether, methyl and ethyl alcohols, acetone, and in dilute sodium carbonate and caustic alkali solutions. The silver and lead salts were obtained, but only the latter were suited to analysis, as the former gave varying results even when the determinations were made in diffused artificial light. Found: (rubber) Pb, 19.0, 18.8 [$C_{48}H_{74}O_8(CO_2)_2Pb$ requires Pb, 19.3%]; (gutta-percha) Pb, 17.2, 17.1 [$C_{48}H_{70}O_{16}(CO_2)_2Pb$ requires Pb, 17.3%]; (balata) Pb, 17.6, 17.5 [$C_{48}H_{74}O_{14}(CO_2)_2Pb$ requires Pb, 17.7%].

Action of Hydrogen Peroxide on the Acetates.—The acetates were still unsaturated and were oxidized further with 100-vol. hydrogen peroxide. The method and procedure were similar to those employed in the oxidation of the hydrocarbons, save that there was no necessity to use chloroform as solvent, since the acetates were soluble in glacial acetic acid.

The new products, which were purified by fractional precipitation from alcoholic solution with ether, in which the original acetates were the more soluble, were colorless amorphous solids, insoluble in water, benzene, toluene, carbon tetrachloride, and

light petroleum, sparingly soluble in ether, and very soluble in methyl and ethyl alcohols, acetone, chloroform, and ethyl acetate. They were saturated, non-acidic and non-reducing, and decomposed on distillation, yielding dark oily distillates. They contained hydroxy- as well as acetoxy-groups, but no alcoholic derivatives suitable for characterization were obtained. Treatment with methyl sulfate and caustic alkali at a low temperature did not effect methylation, and when the temperature was raised resinification occurred. Found: (rubber) C, 54.0, 54.2; H, 5.9, 5.9 ($C_{53}H_{76}O_{32}$ requires C, 54.2; H, 5.9%); (gutta-percha) C, 54.4, 54.8; H, 5.7, 5.7 ($C_{66}H_{84}O_{36}$ requires C, 54.5; H, 5.8%); (balata) C, 54.6, 54.4; H, 5.7, 5.7 ($C_{66}H_{84}O_{36}$ requires C, 54.5; H, 5.8%).

Acetate II	Acetyl Content		Hydroxyl Content	
	Found, %	Calc., %	Found, %	Calc., %
Rubber	16.2, 15.9	13.4	10.7, 10.7	10.6
Gutta-Percha	23.0, 22.9	23.7	4.5, 4.5	4.7
Balata	23.0, 22.8	23.7	4.5, 4.5	4.7

Hydrolysis of the New Acetates.—This was effected by treatment for several hours at 40° with aqueous baryta. The alcohols thus produced resembled the parent acetates very closely, and considerable difficulty was experienced in obtaining a workable method of separation. By continued fractional precipitation from alcoholic solution with ether, three products, very closely resembling one another, were obtained. They were colorless amorphous solids, similar in solubilities to the parent acetates, and were saturated in character. Found: (rubber) C, 53.3, 53.3; H, 6.2, 6.1; OH, 17.0, 17.7; (gutta-percha) C, 53.3, 52.7; H, 6.1, 6.1; OH, 18.4, 18.5; (balata) C, 53.8, 53.3; H, 6.0, 6.0; OH, 18.1, 18.0 ($C_{50}H_{65}O_{28}$ requires C, 53.7; H, 6.1; OH, 18.3%).

These substances were treated with chromium trioxide in glacial acetic acid solution in the manner previously described, but no trace of an aldehydic or ketonic product could be obtained. Treatment with Beckmann's mixture (potassium dichromate and sulfuric acid) yielded products of high molecular weight, devoid of acidic or reducing properties, together with a small proportion of an acid substance of a resinous nature.

Acknowledgment

The authors desire to acknowledge their indebtedness to Professor G. G. Henderson for the continued interest which he has taken in this work; to the Carnegie Trustees for a scholarship which has enabled one of them (J. T.) to take part in this research; to the Imperial Chemical Industries for a grant which defrayed a portion of the expense, and to The North British Rubber Company and Messrs. John Tullis for gifts of raw materials.

Note on the Absorption of Oxygen by Sheets of Rubber

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Very interesting and commercially very important experiments have recently been made in the Bell Telephone Laboratories by G. T. Kohman¹ on the absorption of oxygen by sheets of rubber. No attempt, however, was made to interpret the results mathematically. It is true, of course, that any empirical equation to express the course of the process would be merely a sort of garnish. It would be interesting, however, to show that these processes are not unique.

Some years ago the writer² published an equation which described the progress of many processes in the fields of chemistry, botany, biology, bacteriology, etc. The form of this equation is:

$$C = \frac{C_{\infty} b t^a}{1 + b t^a}$$

It is based upon the results of the tossing of a coin, and represents in fact the law of uni-directional probability. The derivation of the equation is rather lengthy. In this note the equation will be applied to the process of the absorption of oxygen by sheets of rubber.

In the original article cited above the numerical data are not given, but they are so well shown on the graphs that the results may be read off to within one per cent. The amounts of oxygen, therefore, given in the table of this note are expressed in millimeters read off on the original graph, while the time is expressed in hours.

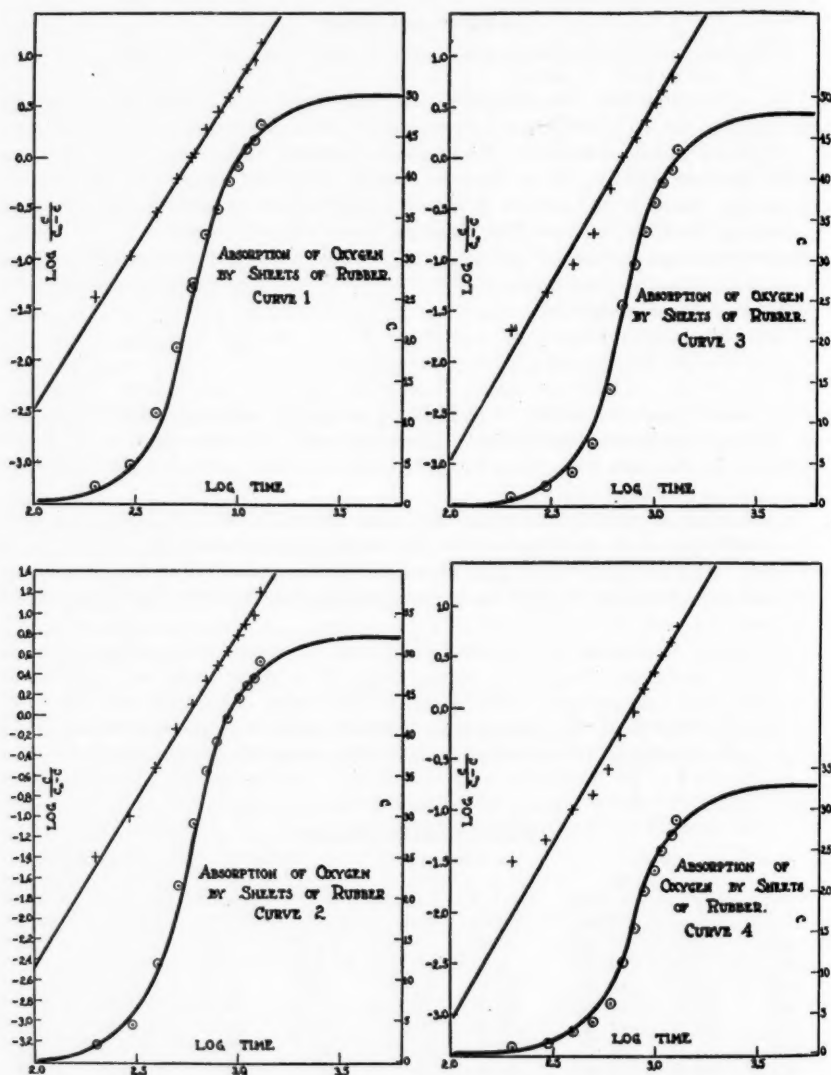
In Table I, C denotes the amount of oxygen absorbed at any time, t , and a and b are constants. Usually, a is the same for a given series of experiments even when the temperature varies, provided the other conditions are the same. However, in this note, the temperatures are the same, but the conditions under which each experiment is conducted are different, inasmuch as the sheets of rubber

TABLE I
Figure 8 (original article)

	Curve 1		Curve 2		Curve 3		Curve 4	
	$a = 3.296$		$a = 3.257$		$a = 3.490$		$a = 3.465$	
	$\text{Log } b = -9.15901$		$\text{Log } b = -8.99790$		$\text{Log } b = -9.94334$		$\text{Log } b = -10.01614$	
t	$C(\text{Obs.})$	$C(\text{Calc.})$	$C(\text{Obs.})$	$C(\text{Calc.})$	$C(\text{Obs.})$	$C(\text{Calc.})$	$C(\text{Obs.})$	$C(\text{Calc.})$
200	2.0	1.30	2.0	1.6	1.0	0.6	1.0	0.3
300	4.6	4.55	4.6	5.5	2.3	2.3	1.6	1.2
400	11.0	10.36	12.0	12.0	4.0	5.8	3.0	3.0
500	19.0	17.65	21.5	19.9	7.5	11.1	4.0	6.1
600	26.5	24.50	29.0	27.5	16.0	16.8	6.5	9.6
700	33.0	31.15	35.5	33.8	24.5	22.6	11.5	13.5
800	36.5	35.90	39.0	38.6	29.5	29.1	15.5	18.9
900	39.5	39.55	42.0	42.0	33.5	33.6	20.0	20.6
1000	41.5	42.15	44.5	44.5	37.0	37.0	22.5	23.3
1100	44.0	44.00	46.0	46.3	39.0	39.6	25.0	25.4
1200	45.0	45.35	47.0	47.6	41.0	41.5	27.0	27.0
1300	46.5	46.35	49.0	48.5	43.5	42.9	28.5	28.3
..	..	50.00	..	52.0	..	48.0	..	33.0

are subjected to different amounts of anti-agers. We should not, therefore, expect a to be the same for all experiments. Still, it does not differ to any great extent, as a glance at the table will show.

The equation in this note is of such nature that from the second differential with respect to $(\log t)$, we obtain the value for C_∞ , since at this point (point of



inflection with respect to $\log t$), $C = C_\infty/2$. In many processes C_∞ is known at the start. For example, in a chemical reaction, C_∞ is the initial concentration of the reacting substance. In other cases, C_∞ is only approximately known and is therefore given more accurately by the point of inflection. This is obvious

from the symmetry of the curve where C is plotted against $\log t$. The straight line plots are obtained by transforming the equation given above into the logarithmic form,

$$\log \frac{C}{C_{\infty} - C} = a \log t + \log b$$

Considering the difficulty of controlling conditions in heterogeneous systems such as these, the agreement between the observed and calculated values is quite satisfactory.

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Coherent Expanded Aerogels

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There are few topics in colloid chemistry that have experienced such extensive investigation as that of the structure of gels. Numerous hypotheses have been presented and supported by experimental data of one character or another. Certain aspects of gels have seemed to classify them as solid solutions, others as emulsions, while yet others give strong support to a two-phase, solid-liquid structure. Although the latter theory in similar form to that postulated by N \acute{a} geli in 1858 has been accepted by most of the foremost colloid chemists, the evidence has not been sufficiently unequivocal to convince all.

The evidence presented in the results of diffusion experiments through gels, the fact that the electrical conductivity, refractive index, and vapor pressure before and after setting are identical, at least in certain cases, and the known facts of syneresis would seem to leave little room for doubt of the two-phase nature of gels in general. A theory in order to be perfectly acceptable must, however, enable verifiable predictions to be made from it.

Thomas Graham¹ showed that the water in silica gel could readily be replaced by organic liquids, and B \ddot{u} tschli² demonstrated the same fact for gelatin. Every biologist takes advantage of this discovery in making microscopic sections. In that process the water is successively replaced from the gelatinous tissues by alcohol, xylene, and paraffin. The final result is a gel in which paraffin is the disperse phase instead of water. In spite of the commonness of this replacement process and the early date of its discovery, very little of a theoretical nature has been made of it. Theories of the origin of swelling in the elastic jellies very commonly ascribe a high place to osmotic forces, but no explanation is offered for the fact that these same gels retain their swelling, and in fact offer great resistance to compression when the water is replaced by a liquid such as benzene in which osmotic forces must be negligible owing to the insolubility of the material of the jelly.

Gelatinous membranes, such as animal membranes, nitrocellulose, and cellophane,³ have frequently been used as ultra-filters. In many cases there can be no question but that the membrane acts as a sieve. It has been conclusively shown that the water in these membranes can be replaced by other liquids without impairing the sieve action.³ The membranous filters have demonstrated particularly well the resistance to compression offered by swollen gels, both in water and in other liquids. Unswollen cellophane will not permit any liquids to pass, and even gases at high pressure pass in scarcely detectable quantities. When it is swollen by merely wetting in water, however, it passes many liquids with ease. In both aqueous and non-aqueous solutions the author has conducted filtrations at as high as 120 atmospheres' pressure with little evidence of compression of the swollen membrane.⁴ An interesting fact is that Rodewald⁵ found that starch swelled against 2500 atmospheres' pressure.

Whatever may be the explanation of swelling, the evidence is indisputable that when many gels are once swollen they show a resistance to compression that is independent of the liquid within their meshes. When once transferred from water to a non-swelling liquid, they show very obvious indifference to what liquid it may be.

In the face of what has been presented, the emulsion theory is completely untenable except, perhaps, in some very special cases, so that no further thought will be given to it.

In spite of the above facts, it can still be argued that the liquid is of large importance in the constitution of the jelly. Many chemists are of the opinion that in the hydrophyle jellies, much of the water is held as shells surrounding the colloid particles. If such were the case, the mobility of the water should be of a different order from that of pure water. That hydration phenomena exist can scarcely be disputed, but the author⁶ has definitely demonstrated that the average viscosity of the water within a gelatin jelly and certain of the inorganic jellies is not widely different from that of pure water. The structure of these jellies, when once formed, is very likely only mildly dependent upon solvation.

Such facts as those above, and others, have led me to the conviction that when once formed, a jelly is in general independent of the fluid filling its meshes, and this fluid might just as well be a gas as a liquid. The fact that all coherent jellies are filled with a liquid is accidental and of little significance.

In support of this assumption, one immediately recalls that silica, alumina, and ferric oxide jellies may be dried to a hard glassy mass which is yet porous, and undoubtedly retains a vestige of the original structure. Even gelatin jelly that has been transferred to alcohol or benzene shows the same phenomenon.⁷ It might be argued that the relationship here is extremely distant. Still a further bit of evidence comes to the support of the assumption. Bechhold⁸ and others have been in the habit of measuring the pore diameter of a membrane for ultra-filtration by means of the so-called bubble test. The membrane is supported with water above it and air pressure applied below until bubbles begin to form on the upper side. From the known surface tension of the water and the measured pressure, the diameter of the pore can be calculated. With number 600 cellophane, copious bubbling occurs at pressures below 70 atmospheres. If the pressure is released, the passages refill with water and it again requires the same pressure to start bubbling. The membrane is found to have suffered no deterioration by the experiment. Now it was shown earlier that a collapsed membrane of cellophane would not permit any gas to pass, so that the only conclusion to be drawn is that the water has been forced out of the meshes of the gel in a small area, and in that region we have a gel with air as the continuous phase.

If one chooses to produce an aerogel by replacing the liquid in a gel with a gas, it is found that as the liquid is evaporated, the gel collapses until it has been reduced to a mass very small compared with the original gel. The very apparent explanation is that as the surface of the liquid tries to recede within the structure of the gel, the capillary effect, combined with the high tensile strength of liquid, crushes the gel to the point where the structure is strong enough to withstand the force. With unhardened gelatin that point is not reached until practically all of the liquid is gone, while with silica and similar gels complete collapse does not occur, and a porous mass remains. Obviously if one wishes to produce an aerogel, he must replace the liquid with air by some means in which the surface of the liquid is never permitted to recede within the gel.

Experimental Procedure

If a liquid is held under a pressure always greater than the vapor pressure, and the temperature is raised, it will be transformed at the critical temperature into a gas without two phases having been present at any time. Actually under these conditions there is no transformation at the critical temperature. The change that does occur is gradual and continuous over the entire range of temperature, and a

small increase in temperature from slightly below the critical temperature to slightly above has no more meaning to a gel in the liquid than a similar change in temperature any other place in the temperature range. Accordingly, it becomes possible to take a gel filled with a liquid, transform the liquid gradually into a gas, allow the gas to expand above the critical temperature, and end with the gel filled with gas of low density without at any time having subjected the gel to compressive forces. This, in general, is the procedure that has been followed in the present investigation. A small autoclave of 75-cc. capacity, capable of withstanding at least 300 atmospheres' pressure, was used. It was heated in an electric furnace.

Results

Swollen rubber is a jelly of a very different nature from all other gels. It would be very interesting indeed if it could be shown that rubber could be converted to an aerogel in the same manner as the aquogels. Immediately, difficulties were met that place rubber in a class by itself. The first step necessary in the formation of an aerogel is the replacement of the swelling solvent by an inactive solvent with a sufficiently low critical temperature. It was immediately found, and the experience is not new, that as soon as it is attempted to replace the swelling solvent with a non-swelling liquid, the rubber shrinks down to its original volume.

My observations would favor the theory that rubber is a two-phase system, one phase being a network or sponge of crystalline fibers and the other being a very viscous liquid held within the network. A swelling liquid would then dissolve in the liquid phase and distend the rubber. The attempt to replace the swelling by a non-swelling liquid would result merely in washing the swelling liquid out of the rubber, rubber and the non-swelling liquid being immiscible.

This theory would predict that if one should swell rubber in such a liquid as ether and then cool to a sufficiently low temperature, the liquid phase of the rubber might be precipitated out on the crystalline skeleton and leave an open gel structure similar to that found in the aquogels. It would then be possible to replace the ether with a non-swelling liquid, *e. g.*, alcohol.

This experiment was tried, cooling the ether gel to the temperature of solid carbon dioxide. As was expected, it now became possible to replace the ether with alcohol, and upon warming to room temperature the alcogel of rubber persisted. In the course of a day or two the rubber had driven out the alcohol and consequently had shrunk to something like its original proportions.

Unvulcanized rubber was used in this experiment. The probabilities are that vulcanization would increase the permanence of the alcogel.

An attempt was made to produce an aerogel by swelling rubber, transferring to liquid carbon dioxide and removing the carbon dioxide above its critical temperature. This undertaking ended in failure, as was expected. The carbon dioxide dissolves in the rubber, and when the pressure is released instead of diffusing out through the meshes of a gel structure it must diffuse through the viscous liquid phase. The consequence was that many gas bubbles were formed within the rubber, and these decreased in size only slowly.

I am of the opinion that a good rubber aerogel can be made by swelling vulcanized rubber, cooling it to the point where good replacement of the swelling by a non-swelling liquid can be effected, eventually filling the structure with such a substance as liquid nitrogen, that has a critical temperature so low that the rubber is still rigid, and allowing the nitrogen to escape above its critical temperature. The surface tension of nitrogen is so low that the rigid rubber gel might not be much compressed if the nitrogen were merely allowed to boil off.

One possibility remains untried. Rubber gels formed by vulcanizing rubber

solutions are reported to synerize. If such is the case, it is very likely that the vulcanization has produced the open sponge structure, and that with these gels replacement of the solvent can be effected without recourse to low temperatures.

A remark should be made on the effect of rewetting and drying aerogels. In the case of each organic gel, water drew itself through in a few minutes, and the wet gel was then more or less transparent. On drying, the gel shrank to a small horny mass. Directly wetting the inorganic aerogels was usually disastrous, the gel being crushed. On the other hand, if the aerogel was left in saturated vapor until it had had time to partially fill with water, it could then be placed in liquid water with no harm. Subsequent drying caused large shrinkage, but usually not to the point to which the original aquogel would have shrunk had it been dried. The greater strength of the gel after it has been converted to an aerogel is doubtless due to dehydration of the fibrils.

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The Law of Absorption of Carbon Dioxide by Rubber as a Function of the Time

C. Chéneveau

The Absorptiometer

It is a well-known fact that rubber absorbs different gases and carbon dioxide in particularly large proportions.

With a view to determining the law of absorption of this gas, the author devised a small absorptiometer which requires only a small quantity of the substance and which can be utilized for other studies of the same kind. The apparatus is entirely of glass consisting of a bottle, F (Fig. 1), of about 30-centimeter capacity

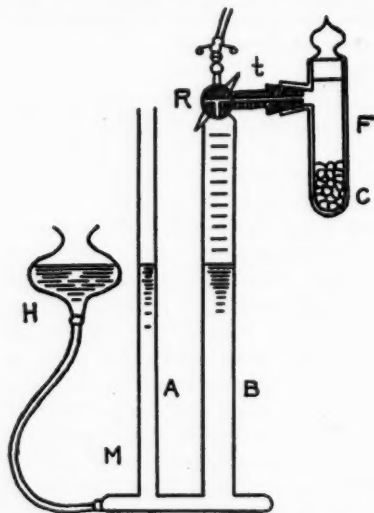


Figure 1

connected by a carefully ground tube, *t*, to a small mercury manometer, M. One of the arms, B, is calibrated and graduated from 0 to 15 centimeters in tenths of a centimeter. These divisions can be estimated to a tenth.

Bottle F can be immersed in a vessel filled with water, so that the temperature is known.

Ten grams of rubber cut into small pieces are put in bottle F, and the bottle and the calibrated manometric tube B are filled with dry carbon dioxide at atmospheric pressure.

If it is desired to determine the law of absorption as a function of the time, the volumes of gas absorbed are measured at definite times at the prevailing temperature and atmospheric pressure. To this end, at each reading the mercury is brought to the same level in the two arms of the manometer by means of reservoir H containing mercury which can be displaced vertically at will rapidly or slowly by means of a moving support.

If it is desired to determine the total quantity of gas absorbed, the operation and the reading are made only at the beginning and the end of the experiment.

Study of the Law of Absorption

To establish this law on a theoretical basis, it may be assumed that the weight of carbon dioxide absorbed, dq , is proportional (1) to the time dt during which absorption takes place, and (2) to the quantity of gas remaining to be absorbed at a given time; the proportionality coefficient k depends upon the rubber under investigation.

If q_0 is the final weight of carbon dioxide absorbed and q the quantity at time t , then

$$dq = k(q_0 - q)dt$$

or as q_0 is constant:

$$d(q_0 - q) = -k(q_0 - q)dt$$

The minus sign indicates that the longer the time, the smaller is the quantity to be absorbed.

Integrating:

$$\frac{d(q_0 - q)}{q_0 - q} = -kdt$$

there is obtained the equation:

$$\log_e(q_0 - q) + \log_e C = -kt$$

when $t = 0$ and $q = 0$, $C = -q_0$, and

$$\log_e(q_0 - q) - \log_e q_0 = -kt$$

or

$$q = q_0(1 - e^{-kt})$$

Verification of the Law

This law which was found experimentally has been verified by all the measurements at 20° and normal atmospheric pressure ($H = 76$ cm. Hg).

The absorption increases with the pressure but diminishes with an increase in temperature.

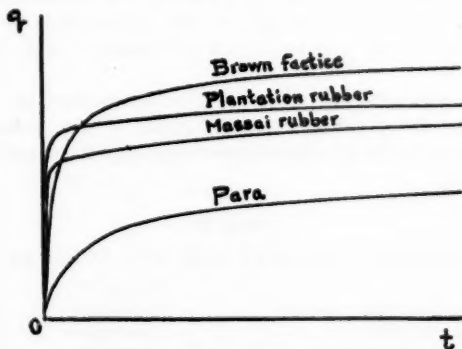


Figure 2

To test the precision of the absorptometer, the quantity of carbon dioxide absorbed by 100 grams of water under the same conditions was determined, and it was found to be 0.167 gram, compared with the value of 0.169 gram in the solubility tables of Bohr and Bock.

TABLE I

Para (of Borneo) Rubber

$$q = 0.140 (1 - e^{-0.437t})$$

t (in Min.)	Calculated (Gram)	Observed (Gram)	Difference in %
10	0.113	0.113	0
15	0.121	0.123	1.5
30	0.130	0.131	0.7
60	0.135	0.135	0
240	0.139	0.139	0
1005	0.140	0.141	0.7

Massai (Africa) Rubber

$$q = 0.134 (1 - e^{-0.355t})$$

t (in Min.)	Calculated (Gram)	Observed (Gram)	Difference in %
10	0.104	0.104	0
25	0.122	0.120	1.6
55	0.127	0.127	0
115	0.130	0.129	0.8
235	0.132	0.131	0.7
975	0.133	0.133	0

Plantation Rubber

$$q = 0.166 (1 - e^{-0.085t})$$

t (in Min.)	Calculated (Gram)	Observed (Gram)	Difference in %
10	0.076	0.076	0
25	0.109	0.113	3.4
55	0.138	0.138	0
90	0.147	0.151	2.6
235	0.159	0.159	0
1425	0.166	0.160	3.5

The results verify the law in the case of three rubbers (cut up into small pieces), as shown in the curves of Fig. 2 and in Table I. The results also give the value of the absorption coefficient for weights of dry carbon dioxide absorbed by 100 grams of rubber under the conditions of temperature and pressure indicated (see Table II).

The absorption coefficients can, moreover, be determined by calculation with a mean approximation of ± 2 per cent, with the aid of two measurements, one ten minutes and the other four to five hours after beginning the experiment and without waiting for saturation.

TABLE II

Absorption Coefficient $\theta = 20^\circ$, $H = 76$ Cm. Hg

	Average of	q	(Gram)
Rubber, Para (Borneo) (cut into pieces)	3 samples	0.147	0.002
Rubber (Massai) (cut into pieces)	2 samples	0.135	0.001
Rubber, Plantation (cut into pieces)	3 samples	0.165	0.001
Rubber, Para (Ceylon) (cut into pieces)	2 samples	0.124	0.002
Rubber, Para (Amazon) (cut into pieces)	1 sample	0.115	0.002
Rubber, Para (Amazon) (crude)	2 samples	0.145	0.002
Rubber, Para (Ceylon) vulcanized (3%)	2 samples	0.168	0.001
Factice, brown	2 samples	0.173	0.002
Factice, white	2 samples	0.150	0.002

Some Interesting Conclusions

1. As the form of the curves shows, factice does not appear to obey the law for rubber. Calculations give values which, in relation to the observed values, show deviations of 8.5 per cent for brown factice and 13.7 per cent for white factice, whereas Table I gives smaller deviations for the different rubbers.

2. Crude rubber absorbs more than the same rubber cut into pieces, which indicates that the latter has become less porous. The absorption measurements can therefore give an idea of the porosity. It is a curious fact that if crude or cut-up rubber is boiled with alcohol the same value for the coefficient of absorption is obtained.

3. Vulcanized rubber or rubber mixed with mineral or organic fillers absorbs carbon dioxide in the same way.

4. Although Reyhler has assumed that carbon dioxide dissolves in rubber, it should be noted that the law of the phenomenon of absorption is identical to that of monomolecular chemical combination. Might there not be formed therefore a compound with one of the components of the rubber?

In any case, it is extremely difficult to remove the carbon dioxide from rubber, even after subjecting it to a vacuum for a long time. Moreover, if successive experiments are repeated on a single sample, it is found that the coefficients of absorption become smaller and smaller. This indicates that more and more carbon dioxide remains in the rubber. The coefficient of absorption for plantation rubber at the end of four tests changed from 0.165 to 0.141 and did not regain its value at the end of 50 days' standing. Upon washing the rubber at this stage, traces of carbon dioxide were detected in the wash water by means of lime water.

5. The study of the k coefficients, which may be called diffusion coefficients, likewise gives information about a rubber.

6. A sample left for one whole day in carbon dioxide did not appear to have altered, as judged by its elongation and tensile strength.

7. Without desiring to draw any definite conclusions from this work, it is believed that more complete tests such as those described would doubtless be of value in obtaining information about the constitution or the quality of different rubbers.

Further Studies of Rubber Solutions

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In a previous communication (*Trans. Inst. Rubber Industry*, 3, 259 (1930)) the measurement of the surface tension of solutions of rubber has been described. One of the conclusions drawn was that mastication of rubber in air is dependent upon two factors: (a) mechanical action, such as is produced by mixing machinery, and (b) absorption of oxygen.

An explanation was put forward, indicating that the increased surface tension of a solution of masticated rubber over a comparable solution of non-masticated rubber is due to the formation of a compound between the rubber and oxygen. The conclusion was also drawn that the electric charge produced during milling is responsible for activating the oxygen prior to the reaction of the latter with the rubber.

The present communication describes further attempts to elucidate the mechanism of mastication.

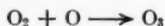
The conclusions outlined above have been confirmed by Cotton (*Trans. Inst. Rubber Industry*, 6, 487 (1931)) and by Busse (*Am. Chem. Soc., Division of Rubber Chemistry*, 1931, *Abstract in India-Rubber Journal*, September 5, 1931, p. 11).

Cotton, by masticating rubber in various gases, showed that oxygen is essential to mastication. He also noted the formation of volatile oxidation products during mastication in air and oxygen, and suggests a very probable reason for their production. Busse has demonstrated the formation of peroxides in the milling process and emphasizes the activation of the oxygen by electric charges. He also confirms the greater effect of cold milling over hot milling in the production of oxidation products.

One of the gases used by Cotton in his mastication experiments was ozonized oxygen, and the results showed that no increase in efficiency of the mastication process was obtained thereby. It therefore seems that the activation of oxygen is not a formation of ozone with subsequent action between the ozone and rubber. An alternative explanation is available. The formation of ozone involves a primary process of activation and ionization:



followed by secondary reactions among which is:



It would seem more reasonable to expect direct action between the rubber and the oxygen atoms produced in the primary process. A low concentration of oxygen in the rubber, as obtains in rubber exposed to the atmosphere, is unfavorable to ozone formation, whereas there is every opportunity for reaction between oxygen atoms and the rubber.

To test these suggestions the following two experiments were tried:

1. Ozonized oxygen was passed over unmasticated shredded pale crepe for varying periods of time, at both ordinary temperatures and 100° C. This is con-

veniently performed by placing the rubber in the inner tube of a Liebig condenser, and the jacket may be used for temperature control.

It was found that ozonized oxygen converted the surface of the pale crepe into a brown resinous substance. This product appeared the same in both experiments, but was formed more rapidly at 100° C. A small piece (1 g.) of this crepe, milled for a few moments to obtain homogeneity, was used for a measurement of refractive index. The value of n_D at 20° C. was 1.5226. In view of the constancy of the refractive index of rubber during prolonged mastication in air (*vide infra*) it appeared that the action of ozonized oxygen on rubber and the action of oxygen in the milling process are not identical. Were there a close resemblance, some change in refractive index would make its appearance after a considerable period of mastication in air.

2. An attempt was made to expose rubber to an atmosphere of oxygen ions. A sheet of pale crepe (about 3 g.) was placed in an x-ray tube, so that, while it was not likely to become heated, it would still be in a favorable position to meet ionized oxygen. The "leak" of the tube was connected to a supply of pure oxygen, and the tube and connections were washed several times with the gas. The tube was then run on the "soft" side, that is, with the oxygen at a relatively high pressure, to obtain as high a concentration of oxygen as was possible.

After five hours' continuous exposure to the gases in the tube, the rubber was removed, and a solution made in benzene (2 g. in 20 cc. of benzene). The appearance of the rubber immediately after the experiment is perhaps worthy of note. The surface remote from the wall of the tube had changed from the usual "dry" appearance of pale crepe to a self-adhesive condition. Further, there was a slight darkening in color, and this darkening was more pronounced in position corresponding to the lilac-colored bands formed by the discharge in the tube.

The surface tension of the solution, however, only showed an extremely small rise, thus:

Solution of unmasticated rubber	28.86 ergs per sq. cm.
Solution of exposed rubber	28.92 ergs per sq. cm.

This difference is within the limits of experimental error, and no positive conclusion may be drawn. The appearance of the rubber, however, indicated that some effect had been produced, but being purely a surface effect, any changes were too small to be measurable.

Measurement of Some Physical Properties

Determination of the following physical properties of raw and masticated rubber were made: (1) refractive index, (2) dielectric constant, (3) surface tension, (4) acetone extract, and the materials employed in the experiments were prepared by the methods described hereunder.

Rubber.—The rubber was first latex pale crepe, which had been kept in a vacuum desiccator for three weeks.

The mastications were carried out in a small experimental mill (rolls 9 in. \times 4½ in.) under conditions as comparable as possible, with a full flow of water through the rolls. Roll temperature was between 15° and 17° C. It was observed that the temperature of the rubber rose in the first few minutes of milling to about 30° C., and subsequently fell to roll temperature after about 15 minutes. This initial temperature rise, due to mechanical working, cannot be avoided, as, until the rubber is sufficiently adhesive and plastic to make good contact with the rolls, the heat cannot readily be conducted away.

The quantity of rubber taken for each mastication was 150 g., the minimum to

provide a thin layer on the front rolls, as well as a "bank" of about one-half inch in diameter.

Benzene.—Recrystallized benzene (b. p. 80.8° C.) was dehydrated by standing, with frequent shaking, over anhydrous sodium sulfate for three weeks.

The solutions of milled rubber in benzene were stored in the dark.

1. *The Refractive Index of Rubber.*—The refractive index of a substance is easily determined to an accuracy of 1 in 10,000, and is employed as a criterion of purity. Therefore if, during the mastication of rubber in air, a compound is formed by the action of oxygen on rubber, its presence should be indicated by a change in the refractive index of the rubber, as mastication proceeds. This is dependent upon the formation, in sufficient quantity, of oxidation products with refractive indices different from the refractive index of rubber.

The refractive index of raw rubber has been previously recorded by several investigators. Twiss (*Inst. Rubber Indust. Year Book*, 1923, 295) obtained a value $n_D = 1.525$ at 15° C. Subsequent measurements by various workers have produced results (summarized by Staudinger and others (*Helv. Chim. Acta.*, 13, 1349 (1930)) which are somewhat lower than that of Twiss, viz., 1.5222 and 1.5219 for n_D at 16° C. These latter give good agreement with a value, 22.56, calculated for the molecular refractivity.

The present results were obtained at 20.8° C., and give excellent agreement with that of Twiss (*loc. cit.*).

TABLE I

Period of Mastication	Refractive Index
15 minutes	1.5248
30 minutes	1.5248
45 minutes	1.5249
60 minutes	1.5249
165 minutes	1.5249
210 minutes	1.5248
330 minutes	1.5249

From these results the molecular refractivity M_D is found to be 22.63, the density of the rubber being 0.921. It is suggested that the calculated value for M_D should be 22.78, obtained by using 1.88 for the double bond constant. Eykmann (*Weekblad*, 3, 706 (1906)) gives this as the value for the double bond in the structure $R_2C=CHR$, which structure corresponds closely to the unit composing the rubber hydrocarbon chain.

It is evident from the above results that the effect of the oxygen is too small to produce any variation in the refractive index.

Y. Tanaka (*Trans. Inst. Rubber Industry*, 2, 330 (1927)) obtained the following results, which indicate a decrease in the refractive index of rubber as mastication proceeds.

Period of Mastication	Refractive Index
0 minute	1.5205
10 minutes	1.5185
20 minutes	1.5150

Possibly the discrepancy in the results of Tanaka and the author is due to the former having used dried solutions, and that the last traces of solvent had not been removed before the index was measured. The author made all measurements directly on masticated rubber.

The Refractive Index of Solutions of Rubber.—Solutions in 180 cc. of pure benzene

TABLE II

Period of Mastication	Refractive Index
0 minute	1.5059
15 minutes	1.5059
30 minutes	1.5059
45 minutes	1.5060
60 minutes	1.5058
165 minutes	1.5060
210 minutes	1.5057
330 minutes	1.5051
Rubber solution exposed to ultra-violet light	1.5059

of 10 g. (± 0.01 g.) of rubber masticated for varying periods in air, gave the above refractive indices at 20.8°C .

Each of these results shows that an application of the additive mixture law holds only very approximately for rubber solutions. Had the law held, its application would have been justified in determining the dielectric constant of masticated rubber from measurements of dielectric constant on the solutions (see below). The reason for the divergence from the law is very probably the high solvation of the rubber particles. With regard to the latter, it is to be observed that there is no change in the refractive index of the solutions with the period of milling of the rubber. If the extent of solvation of the rubber had varied with the extent of mastication, there should have been a progressive change in refractive index in Table II. The absence of any such change confirms the conclusions of Staudinger and Nodzu (*Helv. Chim. Acta*, 13, 1350 (1930)) in which the inference is drawn from viscosity measurements that homopolar colloidal molecules are solvated to approximately the same extent.

2. *The Dielectric Constant of Rubber Solutions.*—Solutions of rubber in benzene were prepared by dissolving 10 g. (± 0.01 g.) in 180 cc. of benzene (= 5.97 per cent by weight).

A solution was also prepared of the same strength of unmasticated rubber. This was exposed in a quartz flask to the mixed radiation from an ultra-violet lamp for 24 hours. No precise measurement of the radiation was possible, but the reduction of viscosity of the solution was considerable.

The dielectric constant of these solutions was then measured, employing a Hartley circuit (see Appendix). The method had been previously checked by using standard liquids. Both benzene and conductivity water gave very close agreement with the accepted values for their dielectric constants. The accuracy was of the order of 1 in 500. After each reading, the condenser dipping in the rubber solution was well washed with benzene and dried, and before taking a reading on any rubber solution air bubbles between the vanes of the condenser were removed. The measurements were made at room temperature 14 – 17°C ., were repeated in the same order as a check, and are given in Table III.

While the method employed is considered highly accurate, it is not thought

TABLE III

Period of Mastication	Dielectric Constant
0 minute	2.31
15 minutes	2.31
30 minutes	2.36
60 minutes	2.53
165 minutes	2.41
210 minutes	2.41
330 minutes	2.44
Solution exposed to ultra-violet light	2.36

justifiable to assume the same accuracy for a benzene solution of rubber, owing to the unavoidable loss of solvent. An accuracy of 1 per cent is considered reasonable.

The results are plotted in Fig. 1. The curve for the dielectric constant of solutions of masticated rubber, plotted against the period of mastication, shows indications of a maximum value for the dielectric constant, although there are not sufficient points to ascertain definitely the position of the maximum.

The results for 210 minutes and 330 minutes show a slow rise in dielectric constant of the solution, and hence, therefore, of the rubber. This point, together with the significance of the maximum value in the curve, is discussed later.

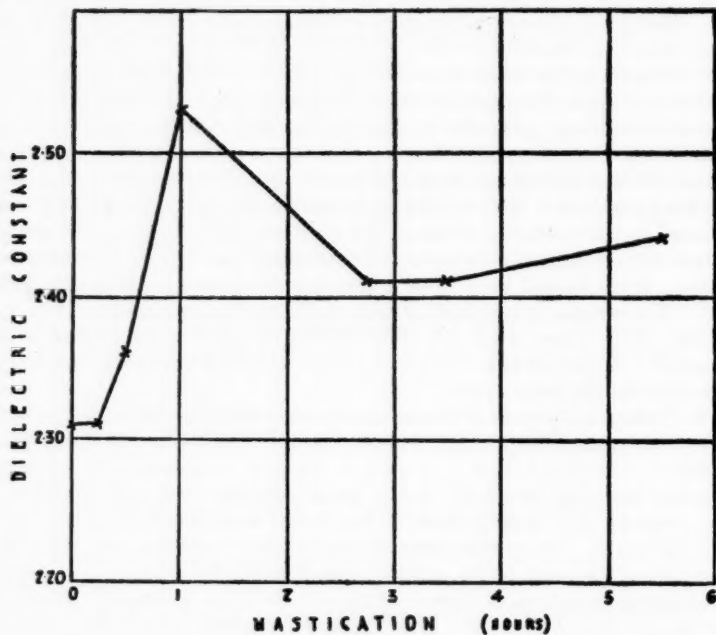


Figure 1

It was hoped that a measurement of the dielectric constant of comparable solutions of rubber in benzene would enable the dielectric constant of the masticated rubber to be calculated. Debye ("Polar Molecules," 1929) has shown that while the dielectric constant of mixtures of two pure liquids varies in an apparently arbitrary manner with the percentage composition, the additive mixture law holds for small proportions (up to about 10 per cent) of one component. The failure of the additive mixture law to hold for refractive indices of rubber and its solutions in benzene precludes the possibility of any determination of the dielectric constant of masticated rubber.

3. *The Surface Tension of Rubber Solutions.*—Attempts to follow the process of mastication in air were also made by measuring the surface tension of solutions in benzene of rubber masticated for various periods on cold rolls. The solutions were made of 10 g. (± 0.01 g.) of the rubber dissolved in 100 cc. of pure dry benzene.

The method of measurement employed was the same as that previously described (Shacklock, *loc. cit.*), and the surface tension of a solution of unmasticated rubber is taken as 28.86 ergs per sq. cm.

TABLE IV

Period of Mastication	Surface Tension
25 minutes	29.86 ergs per sq. cm.
40 minutes	30.20 ergs per sq. cm.
60 minutes	30.52 ergs per sq. cm.
100 minutes	30.58 ergs per sq. cm.
150 minutes	30.53 ergs per sq. cm.
200 minutes	30.00 ergs per sq. cm.
300 minutes	30.34 ergs per sq. cm.

The results given in Table IV were obtained, and are plotted in Fig. 2.

With increasing periods of milling up to about 80 minutes, there is a rise in the surface tension, and subsequently the latter remains constant. This result appears surprising, and in the continuous absorption of oxygen noted by Cotton (*loc. cit.*) a roughly parallel rise in surface tension would be expected. It must be remembered, however, that surface tension indicates only surface effects, and these are dependent upon concentrations in the bulk of the solution according to the Freundlich adsorption equation.

Further, surface tensions of aqueous solutions of fatty acids show greater variation in surface tension with concentration when the active solute differs greatly from the solvent in chemical constitution (Freundlich, "Capillary Chemistry," p. 64). It therefore appears possible that the surface tension of masticated rubber solution is affected only by oxidation products of low molecular weight, *i. e.*, relatively high oxygen content. Oxidation products which are of higher molecular weight will probably contain a smaller percentage of oxygen, *i. e.*, be more nearly hydrocarbon in structure, and hence will produce little effect on the surface tension.

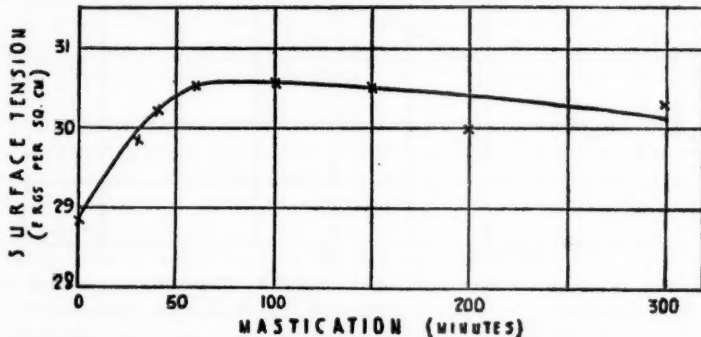


Figure 2

4. *Acetone Extraction of Masticated Rubber.*—It is probable that the oxidation of rubber produces fatty acids, or substance chemically allied to fatty acids. The acetone extract of masticated rubber will therefore be expected to contain these substances.

Accordingly, rubber which had been masticated as described for a known period of time was extracted with acetone for fifty hours. The amount of the extract was determined by weighing, and the results are given in Table V, and plotted in Fig. 3.

In making these extractions, 10 g. of masticated rubber were used. As the period of mastication lengthened the rubber became increasingly plastic and adhesive, as at the temperature of extraction (boiling acetone = 56°C.) most of the samples quickly settled to the bottom of the extraction thimble. In these circumstances, it was impossible to guarantee complete extraction even after 50

TABLE V

Period of Mastication	Acetone Extract, Per Cent
20 minutes	2.19
40 minutes	2.33
60 minutes	2.30
100 minutes	2.38
150 minutes	2.47
200 minutes	2.53
300 minutes	4.61 (?)

hours. Preliminary experiments showed that it was advisable to take as much as 10 g. of the rubber, since the amount of extract increased but slowly with time of mastication.

These results may be considered to be relative, but not quantitative, though it would be expected that such a long period of extraction would remove most of the acetone soluble material. The extraction of rubber masticated for 300 minutes shows a marked difference from the previous results. In this experiment only a small quantity of material was available, and the error is correspondingly greater.

The results do not show a straight line proportionality between the time of milling and the percentage of acetone extract. The rate of production of extractable matter appears to fall off as the time of mastication increases. In view of the

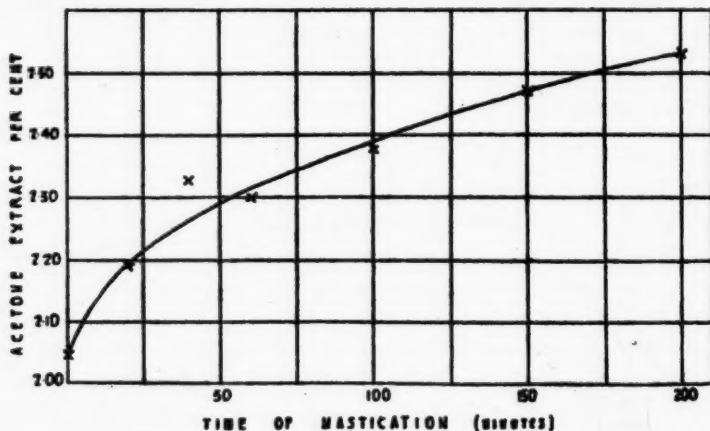


Figure 3

almost straight line proportionality between period of mastication in air, and increase in weight of masticated rubber, as shown by Cotton, the present results point to some oxygen being added on to the rubber and not merely reacting with the hydrocarbon chains, and forming oxidation products.

Discussion of Results

While the absorption of oxygen by rubber during milling in air appears an undisputed fact, the behavior of the oxygen when absorbed has not hitherto been elucidated. Porritt and Fry (*Trans. Inst. Rubber Industry*, 3, 203 (1927)), from measurements of viscosities of solutions of raw rubber, conclude that chemical reaction occurs between rubber and oxygen when the former is heated in air.

Disaggregation of rubber during mastication has been inferred by many investigators. Grenquist (*Ind. Eng. Chem.*, 22, 759 (1930)), from plasticity measurements, concluded that a thermal disaggregation of rubber occurred when heated

in steam, and this was followed by a reaggregation on standing. The author (*loc. cit.*) has assumed disaggregation, as distinct from depolymerization, when rubber is milled in air, as no change in surface tension of comparable solutions of air-heated and untreated rubber was observed.

However, Cotton (*loc. cit.*) by mastication in nitrogen showed from plasticity measurements that most probably rubber completely free from oxygen will undergo no change on mechanical treatment. In view of the simplicity of this experiment, the conclusion is highly significant.

Staudinger and co-workers (*loc. cit.*) from viscosity measurements have concluded that the molecular weight of masticated rubber is considerably less than that of unmasticated rubber, while Busse (*loc. cit.*) also infers a breaking down of long molecules into shorter ones during milling.

It therefore appears that the absorption of oxygen is essential to the disaggregation of the rubber hydrocarbon.

The results in the present paper support this conclusion.

The most probable structure to be attributed to raw, unmasticated rubber, at the present time, is what Whitby (*Trans. Inst. Rubber Industry*, 5, 184 (1929); 6, 40 (1930)) calls a "polyphase" system, consisting of a range of high polymers of isoprene, the particle being long chains of isoprene units linked by primary valences. There is no definite evidence for the chains having uniform length, and it is also probable that these chains by their unsaturated valences, are joined together side by side, forming micelles. Such a structure, either chain or micelle, is non-polar.

The results of measurements of the dielectric constants of solutions of milled rubber are explained in the following manner: During the initial stages of mastication, the oxygen already dissolved in the rubber becomes activated by the electric charge produced, and then reacts with the rubber. The reaction will presumably occur at the nearest unsaturated linkage. As the oxygen becomes used up, more dissolves in the rubber.

If the linkage attacked by the rubber is near the end of a long hydrocarbon chain, a molecule of oxidation product will be split off; if, however, it be anywhere except in the center of mass of the chain, a polar structure will be developed by addition of the oxygen. The formation of a polar structure results in a rise of the dielectric constant.

For some little while the continuous addition of oxygen to the rubber will continue to increase the polarity of the rubber as a whole. Gradually, however, the polarity is reduced, as with further oxygenation the long molecules will possess a less unsymmetrical structure, until finally, on the average, the polar moment has been reduced considerably. A fall in dielectric constant should therefore follow the initial rise.

The continuous absorption of oxygen will manifest itself after the polar structure has largely disappeared, producing a slow change, most likely to rise in the dielectric constant. The last two results in Table III suggest this.

It is conceivable that the addition of oxygen to an unsaturated linkage may weaken mechanically the strength of the hydrocarbon chain. If this is so, the breaking of the molecules by milling as suggested by Busse (*loc. cit.*) is explained. If the micelle structure attributed to rubber be considered, the disaggregating effect may be explained by the addition at unsaturated linkages as above, the combination with the oxygen tending to reduce the unsaturated valences, and, therefore, to weaken the binding forces holding the micelle together, and permit of disaggregation by mechanical action. Dogadkin and Pewsner (*Kolloid-Z.*,

53, 239 (1930)), from viscosity measurements infer that during the milling of rubber, colloid chemical processes of disaggregation of rubber micelles occur, as shown by a decrease on structure viscosity exponents. Either chain rupture or the breaking down of the micelle explains satisfactorily the lowering of viscosity of solutions of milled rubber.

The results of the measurement of the surface tension of solutions of milled rubber show a rise, with increasing time of milling, and subsequently an almost constant value. It would at first appear that such a change should follow approximately, if not closely, the increase in acetone extract. This, however, does not take place. The products of the oxidation of raw rubber during mastication may be surmised, but are not known. It is suggested that the surface tension of solutions is increased by the oxidation products formed in the earlier stages of the mastication, possibly as a result of the oxidation of the end groups of the hydrocarbon chains. In the subsequent stages of milling the oxidation products are different, more hydrocarbon in character, and are thus much less likely to produce surface effects.

Conclusions

1. The refractive index of rubber is not appreciably affected by mastication for five hours in the cold.
2. The refractive index of solutions of rubber indicates that solvation of the rubber hydrocarbon is independent of the time of milling of the rubber.
3. The oxygen, which is continuously absorbed by rubber during mastication in air, reacts with the rubber, evolving oxidation products, and also forms addition products. It is suggested that this addition of oxygen reduces the micellar binding forces and so permits easy mechanical disaggregation.
4. The acetone extraction of rubber increases progressively with the period of mastication of the rubber.
5. The surface tension of solutions of rubber milled for varying periods increases with the time of milling, and subsequently remains constant. This is possibly due to the oxidation products from the end-groups of the hydrocarbon chains. Such end-groups are more open to attack by oxygen than the rest of the chain; further, there is a limit to the number of end-groups available for reaction (two per chain) while the number of unsaturated linkages between the end groups is undoubtedly many, and each of these is a possible point of oxygen action.

Appendix

The Measurement of the Dielectric Constant.—The apparatus required for the measurement is shown diagrammatically in Fig. 4.

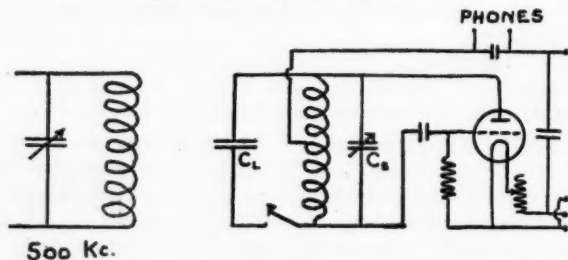


Figure 4

C_S = Sullivan sub-standard condenser.
 C_L = Condenser of capacity approximately 0.0003 mf., for use with the solutions of rubber.

Method.—

- (i) Set C_s at a high reading, and tune oscillator to it.
- (ii) Switch in C_L at minimum capacity, and adjust C_s to find minimum capacity of C_L .
- (iii) Switch in C_L at maximum in air, and adjust C_s to find air capacity of C_L .
- (iv) Immerse C_L at maximum in the rubber solution, and adjust C_s to find capacity of C_L in solution.

Readings of C_s are taken in degrees and the corresponding capacities are read from a calibration curve.

$$\text{Dielectric constant of liquid} = \frac{(\text{iv}) - (\text{ii})}{(\text{iii}) - (\text{ii})}.$$

Studies on Rubber in Solution

I. Studies on the Aging of Rubber Solutions

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It is well known that raw rubber in colloidal solutions with different dispersion mediums shows the general characteristics of aging such as a decrease in its viscosity, whether aged by natural or artificial methods, and especially when exposed to ultra-violet light. Whitby and Jane (*Colloid Symposium Monograph*, Vol. 2, page 16) pointed out this phenomenon, and Asano (*Mem. Coll. Eng. Kyoto Imp. Univ.*, Vol. 3, page 267) noticed that dispersed rubber sols decreased in viscosity and the rubber depolymerized and became insoluble by exposure to ultra-violet light. This effect was particularly noticeable with light of 2250 Å. U.; however, light of longer wave lengths caused oxidation of the rubber and formed a transparent insoluble substance. Recently Hada (*Rubber Ind.*, 1931, 147) demonstrated the curves of decrease in viscosity of rubber sols by exposure to ultra-violet light, and pointed out that the sols reached a definite viscosity after long exposure.

The theory generally accepted to explain the mechanism of the lowering of the viscosity of rubber sols on aging is that depolymerization results from the oxidation of rubber molecules, and thereby increases the degree of dispersion. The process as a whole involves the formation of a dispersed phase from the absorption of the dispersion medium, and after passing the stages of solvation the viscosity of sols thus formed decreases on aging. The principal cause of these phenomena is considered to be due to a change in the structure of the dispersed particles by a chemical change of the dispersed phase itself. Whether or not it is possible to obtain, in the laboratory, a stable rubber sol by the process of long aging is not certain. It is, however, no exaggeration to say that the oxidation of the dispersed phase causes a decrease in its affinity for the dispersed medium, i. e., the oxidation changes the emulsoid to a supersoid or, in other words, there is a decrease in the size of the particles in the dispersed phase if the theory of the aging of rubber sols is that there is an increase in the dispersity by depolymerization.

The author subjected rubber sols to long exposure to ultra-violet light and measured the lowering of their viscosity. The results show that (1) rubber sols in benzene reached a constant viscosity, and (2) the use of different solvents causes marked differences in rubber sols. The Brownian movement of the particles in aged rubber sols was observed with a cardioid ultra-microscope. These experiments were made as a preliminary test to explain the mechanism of dispersion of raw rubber in solvents.

Experiments and Discussion of the Results

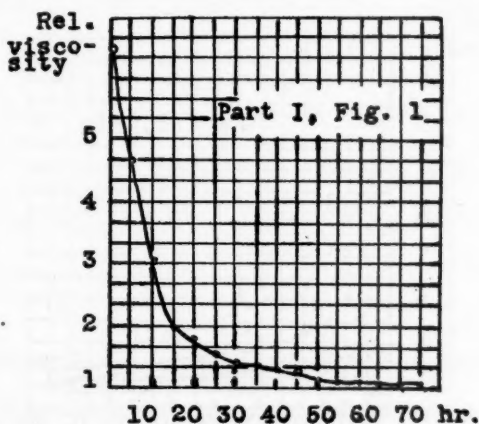
1. Pale crepe which was washed and dried was dissolved in pure benzene and kept in a dark place for 10 days, with occasional shaking. The samples thus prepared were placed in ordinary glass bottles with stoppers and were exposed to ultra-violet light from a mercury arc lamp 50 cm. from the sample (ordinary glass is impermeable to light having a wave length less than 3000 Å. U.). The viscosity was measured by an Ostwald viscosimeter at 20° C. The relative viscosity was calculated against the time of flow of benzene (26.2 seconds). The results, given in

PART I, TABLE I

Ultra-Violet Light Exposure, Hours	Relative Viscosity	Ultra-Violet Light Exposure, Hours	Relative Viscosity
0	6.49	40	1.30
5	4.60	45	1.23
10	3.04	50	1.18
15	1.93	55	1.16
20	1.81	60	1.13
25	1.49	65	1.10
30	1.47	70	1.10
35	1.34	75	1.10

Table I and Fig. 1, confirm past experimental proof that rubber sols decrease in viscosity on aging, such decrease being continuous until a constant value is reached. There was almost no change in the viscosity of the rubber sol when it was kept in the dark without exposure to ultra-violet light for several days.

2. The study of the effect of various solvents on the lowering of the viscosity on aging was made with a 0.5 per cent rubber sol in each of the following: benzene, pure benzene, carbon tetrachloride, tetrachloroethane, trichloroethylene, carbon disulfide, and chloroform. The viscosity of these sols was estimated. To prepare these 0.5 per cent sols, 1.4 per cent rubber solutions were first prepared. After two days these were diluted to 0.7 per cent, and after standing 4 days, any precipitate formed was separated by decantation and the solution was diluted to 0.5 per cent.

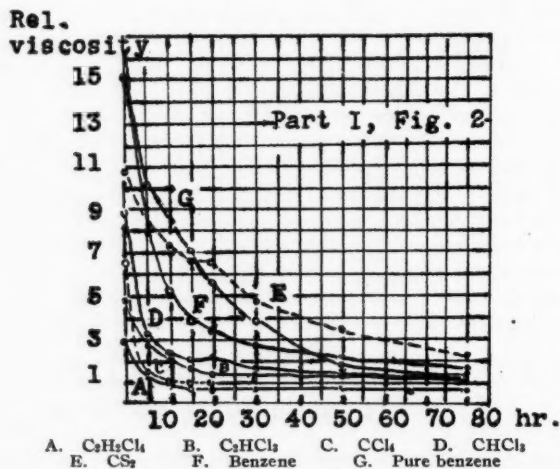


The viscosity was estimated 3 days after preparation. The rubber solutions in trichloroethylene, chloroform, and carbon disulfide were complete, so no decantation was necessary. The solutions in carbon tetrachloride and carbon disulfide were turbid, especially the one in carbon disulfide. The results of the estimation of the relative viscosities of these sols are shown in Table II. There were marked differences in the results among the various solvents. Carbon tetrachloride sols gave a precipitate after 30 hours' exposure to ultra-violet light, and this precipitate turned a yellowish color on further exposure. Carbon disulfide and chloroform sols showed no lowering of viscosity during 15-20 hours' exposure. The aging effect on the carbon disulfide sol was rather small. The carbon tetrachloride sol showed a relative viscosity below 1 after 5 hours' exposure. Still another remarkable fact was that the aging effect on sols in which the dispersion medium contained chlorine was far greater than when the dispersion medium was a pure hydrocarbon, such as

PART I, TABLE II

Time of Exposure to Ultra-Violet Light, Hours	Relative Viscosity						Benzene	Pure C_6H_6
	$C_6H_5Cl_4$	C_2HCl_3	CCl_4	$CHCl_3$	CS_2			
0	2.95	4.94	6.61	8.93	10.61		16.35	15.11
5	1.22	2.68	1.43	3.21	8.34		8.07	10.22
10	0.94	2.01	1.19	2.37	7.28		5.18	8.48
15	0.84	1.66	1.12	2.04	6.55		3.92	6.98
20	0.79	1.48	1.10	2.15	6.56		3.56	5.56
30	0.76	1.47	1.20	1.77	4.84		2.63	3.87
50	0.83	1.31	..	1.39	3.49		2.11	1.89
80	0.71	1.23	..	1.11	2.20		1.68	1.32

benzene and pure benzene. The solvent containing chlorine had a special property of increasing the dispersion of the rubber. Although it is too early to make a definite statement about this experiment, it is considered that the solvents, carbon tetrachloride, carbon disulfide, tetrachloroethane, etc., decompose on exposure to ultra-violet light, and the decomposition products may react with rubber to form an aged rubber. McKenzie and King ("Practical Ultra-violet Light Therapy," p. 100) have already shown that carbon tetrachloride is very sensitive to ultra-violet light, and when exposed liberates free chlorine, which may in turn react with the rubber. Such a phenomenon may also be possible in the case of carbon disulfide



and tetrachloroethylene, but this is beyond the scope of this paper. This would be a chemical change in the rubber molecule, and it would be a good idea to investigate the special properties of these solvents.

3. It has already been discussed that on aging, rubber particles increase in dispersity and decrease in viscosity, in spite of the decrease in the size of the particles. This is attributed to a decrease in affinity of the dispersed phase for the dispersion medium, as a result of oxidation of the dispersed rubber. The sol with the least affinity for the dispersion medium showed most clearly the Brownian movement when viewed with a cardioid ultra-microscope, and the sol which had most affinity for the dispersion medium did not show the Brownian motion. Although Klein and Stamberger (*Kolloid-Z.*, 35, 362) and Toyabe (*J. Soc. Chem. Ind.*

Japan, 33, No. 1) described their observations on the Brownian movement in rubber sols they did not call attention to the fact that the Brownian movement is due to the decrease of affinity of the dispersed phase for the dispersion medium. It is not confirmative to say that the rubber sols decreased their affinity for the dispersion medium because the Brownian movement is visible. However, the author assumes the hypothesis above from the fact that the rubber sol showed a continuous decrease in viscosity on aging.

The observation on rubber sols indicated that they showed no Brownian movement at the early period of dispersion, but it was clearly visible after aging. Although it is not considered that all particles are oxidized and lose their affinity for the dispersion medium at the same rate on aging, it is considered that the dispersed rubber approaches a colloidal solution in the final stage, and this sol has less affinity for the dispersion medium, since it showed the lowest viscosity and most active Brownian movement.

The reason why the Brownian movement is visible in some cases at the beginning of preparation of the rubber sol is explained by the theory that the dispersion of rubber is not uniform, and the smallest particles are oxidized first and lose their affinity for the medium, since the greater the dissolving power of the solvent for rubber, the more rapid is the lowering of the viscosity of the rubber solution.

At any rate, there are marked differences between the colloidal chemical properties of rubber sols which have reached a definite viscosity on aging and those of sols which do not show any aging at all; therefore, a study of these two different sols may throw some light on the mechanism of the dispersion of rubber.

Summary

1. On aging the viscosity of raw rubber sols decreases continuously until it reaches a constant value.
2. Different solvents of rubber give different aging effects, when rubber sols are exposed to ultra-violet light.
3. Increased Brownian movement and decreased viscosity take place with increase in aging.

These facts suggest the theory that rubber sols decrease in affinity for the dispersion medium on aging.

II. Structural Viscosity of Rubber Solutions

The viscosity of colloidal solutions is closely related to the structure of the dispersed phase. The relation between viscosity and pressure (low pressures) shows a deviation from the Hagen-Poiseuille law and is better expressed by the Waale-Ostwald formula: $\eta = KP^{1-n}$, where η is the relative viscosity, and K and n ($n > 1$) are constants depending on the nature of the solution and the conditions of the experiment. Ostwald (*Kolloid-Z.*, 36, 99) called the viscosity of colloidal solutions which agree with the above formula, *structural viscosity*.

Dogadkin and Pewsner (*Kolloid-Z.*, 13, 239) used an Ostwald viscosimeter, with a U tube with a water column attached to measure the air pressure, in determining the viscosity of rubber solutions, and found that the relation between the viscosity of rubber solutions and the pressure can be expressed by the formula: $\eta = KP^{1-n}$, when the height of the water column is below 70–90 cm. By using the exponent n of structural viscosity, they compared the degree of aggregation of the dispersed particles, and observed that there is an increase in the value of n with an increase in temperature, and that the value of n is decreased by milling and on aging.

Kirchhof (*Kolloid-Z.*, 30, 15) indicated that the Poiseuille law can be applied to the estimation of the viscosity of rubber solutions in various solvents when the height of the water column is above 60 cm. He concluded that the viscosities can be estimated at this pressure, and he calculated the volume of the dispersed phase by the use of the Hatschek formula: $A = (\eta/\eta_0 - 1)^3$ (*Kolloid-Z.*, 12, 238). A is the ratio of the total volume of the dispersed phase to the total volume of sol, and η is the relative viscosity. The result agreed well with the solvent power of the various solvents, as discussed by Posnjak (*Kolloid-chem. Beihefte*, 3, 417).

The present paper deals with the dispersion of rubber in various solvents, based on the view of structural viscosity of Dogadkin, and the results are compared with the Kirchhof formula, which expresses the degree of aggregation of the dispersed particles by the exponent n .

Experiments and Discussion

All samples were prepared the same as in the preceding work. The apparatus used was an Ostwald viscosimeter (Fig. 1). The diameter of the capillary tube of

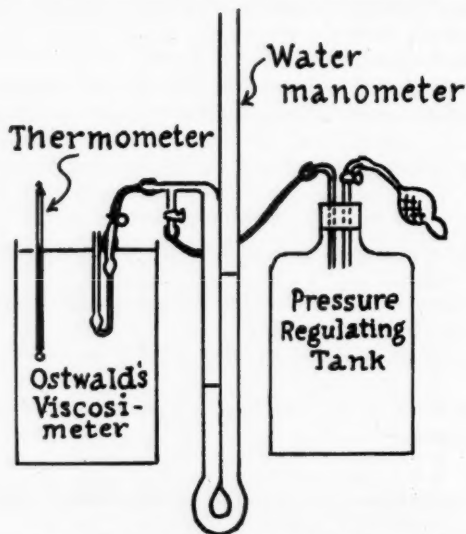


Figure 1—Part II. Apparatus for Viscosity Measurement

the viscosimeter was 0.4 mm., and the pressure in the bottle was kept constant within ± 0.2 cm. error in the height of the water column. The pressure, $P = H + h\rho$, where H is the height of the water column, h is the average difference in fall in the viscosimeter, and ρ is the density of the solvent. The data of the experiments are shown in Table I, and Figs. 2 and 3. The data indicate that the relation between the pressure and the viscosity agrees well with the formula: $\eta = KP^{n-1}$, as in the case of the estimation at lower pressure by Dogadkin, but the agreement between the theoretical value and the experimental value, as well as the value of n , was far better in our experiments than in his. This is in accordance with the theory that n indicates the degree of aggregation of the dispersed particles. The values of n with different solvents are shown in Table II. On the other hand, Kirchhof obtained the volume of the dispersed phase by using Hatschek's formula with the following result. The volume of the dispersed phase of a 0.5 per cent sol

PART II, TABLE I

P	Estimated η	Calculated η	$\Delta\eta$ (%)	P	Estimated η	Calculated η	$\Delta\eta$ (%)
Carbon Disulfide				Trichloroethylene			
22.0	8.29	8.27	+0.24	24.0	6.71	6.83	-1.79
32.0	6.67	6.63	-0.60	34.0	5.81	5.81	0
42.0	5.56	5.64	-1.44	44.0	5.20	5.16	+0.77
52.0	5.00	4.98	+0.40	54.0	4.73	4.69	+0.85
62.0	4.44	4.48	-0.90	64.0	4.39	4.34	+1.14
72.0	4.14	4.11	+0.72	74.0	4.05	4.06	-0.25
82.0	3.79	3.80	-0.26	84.0	3.79	3.82	-0.79
92.0	3.57	3.55	+0.56	94.0	3.62	3.63	-0.28
$n = 1.590, K = 51.22$ Av. -0.01				$n = 1.463, K = 29.68$ Av. -0.05			
Chloroform				Pure Benzene			
24.2	7.66	7.69	-0.39	16.7	9.53	9.49	+0.42
34.2	6.36	6.36	0.00	26.7	7.65	7.58	+0.92
44.2	5.51	5.64	-2.36	36.7	6.54	6.64	-1.53
54.2	4.95	4.93	-0.40	46.7	5.81	5.80	+0.17
64.2	4.47	4.49	-0.47	56.7	5.26	5.29	-0.57
74.2	4.18	4.14	+0.96	66.7	4.93	4.89	+0.81
84.2	3.95	3.86	+2.28	76.7	4.35	4.58	-5.29
94.2	3.53	3.63	-2.83	86.7	4.35	4.32	+0.65
$n = 1.553, K = 44.78$ Av. -0.34				$n = 1.478, K = 36.45$ Av. -0.65			
Tetrachloroethane				Benzene			
25.2	3.82	4.10	-7.33	18.3	13.21	13.34	-0.98
35.2	3.55	3.54	+0.28	28.3	10.59	10.73	-1.32
45.2	3.25	3.18	+2.15	38.3	9.40	9.23	+1.81
55.2	3.04	2.91	+4.28	48.3	8.27	8.22	+0.60
65.2	2.66	2.71	-1.88	58.3	7.48	7.48	0.00
75.2	2.53	2.54	-0.40	68.3	6.92	6.91	+0.14
85.2	2.42	2.41	+0.41	78.3	..	6.46	..
95.2	2.33	2.29	+1.72	88.3	6.08	6.08	0.00
$n = 1.437, K = 16.77$ Av. -0.11				$n = 1.499, K = 57.00$ Av. +0.04			
Carbon Tetrachloride							
25.2	11.26	11.25	+0.09				
35.2	..	9.39	..				
45.2	8.21	8.20	+0.12				
55.2	7.35	7.35	0.00				
65.2	6.81	6.72	+1.32				
75.2	6.27	6.22	+0.69				
85.2	5.79	5.81	-0.35				
95.2	5.39	5.48	-1.67				
$n = 1.542, K = 64.77$ Av. +0.02							

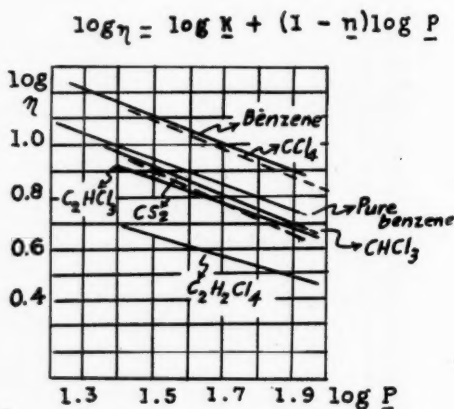
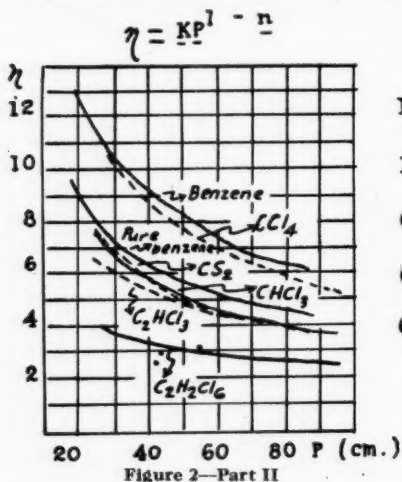
PART II, TABLE II

Solvents	Density	Boiling Pt.	n	K	Whether or Not Decanted
Carbon disulfide	1.26	46.2	1.590	51.22	No
Chloroform	1.49	61.0	1.553	44.78	No
Carbon tetrachloride	1.60	76.6	1.542	64.77	Yes
Benzene	0.87	80.0	1.499	57.00	Yes
Pure benzene	0.70	100.0	1.478	36.45	Yes
Trichloroethylene	1.47	87.0	1.463	29.68	No
Tetrachloroethane	1.60	131.0	1.437	16.77	Yes

of rubber was as follows: carbon tetrachloride > tetrachloroethane > benzene > pure benzene, and concluded that the swelling of the rubber in the solvent is closely related to the degree of dispersion. He further referred to Posnjak's view that the swelling power of rubber in solvents containing chlorine is greater than in pure hydrocarbons, and therefore the size of the dispersed particles in carbon tetrachlo-

ride is smaller than in benzene. Accordingly the volume of the dispersed phase becomes greater because of its greater affinity for the solvent.

Such hypotheses, however, do not agree with the result obtained with carbon tetrachloride in our experiment nor with trichloroethylene. Granting that all these theories are correct, *i. e.*, the solvents containing chlorine have greater dispersing power and greater affinity for rubber, such sols showed a greater rate of decrease in viscosity on aging. It is therefore considered that the disagreement between our result in the case of carbon tetrachloride and trichloroethylene in Kirchhof's formula may be attributed to aging of these sols previous to the experiment. This would affect the decrease of the value of n as in the case of the pre-



ceding experiment. The results of this experiment, like that of Dogadkin and that of the preceding article, should give the following order: pure benzene > benzene > trichloroethylene > carbon tetrachloride > tetrachloroethane.

In order to explain the experiments of Posnjak, Kirchhof, and the author, it is necessary to use the author's hypothesis that the affinity between the dispersed phase and dispersion medium decreases on aging. The most important precaution which should be taken in the experiment is in connection with the conditions of sampling, since these affect directly the aging test.

Summary

1. Experimental proof of the Waale-Ostwald formula by Dogadkin is confirmed on various rubber sols.
2. A comparison between the degrees of aggregation of dispersed particles, expressed by the exponent n of the structural viscosity and the volume of the dispersed phase obtained by Kirchhof (using Hatscheck's formula) was made, and the result is best explained by the hypothesis that the affinity of rubber for the dispersion medium decreases with aging.

III. Note on Rubber Solutions

The rubber solvents which are used for practical purposes are carbon disulfide, chloroform, benzene, and pure benzene. The last two are those most generally used, but carbon disulfide and chloroform are superior when a thin film is wanted.

No one has studied, from the colloidal chemical view, why they are superior for making a thin film, and it is worth while to investigate this from a scientific point of view.

Carbon disulfide forms a uniform solution to the naked eye, and the fact that it has a higher degree of aggregation of dispersed particles is already shown in the exponent n of the structural viscosity. The greater degree of aggregation may be attributed to less depolymerization of the rubber molecules. Such products as overvulcanized rubber depolymerize, which decreases the mechanical strength. Rubber products made from rubber solutions, *e. g.*, rubber films, should have superior quality if they are made with a solvent which does not cause too much depolymerization and yet forms a uniform strong film. Carbon disulfide is the best answer to these requirements.

From the standpoint of the dispersion theory, benzene and pure benzene are inferior to carbon disulfide and chloroform, but they are used for industrial purposes because of their low price and ease of handling. Benzene has the defect of leaving large amounts of insoluble precipitate in rubber solutions, and although this precipitate seems to be decreased by better milling, any such precipitate would leave coarse particles on the film. It has been suggested that the increased solubility of rubber in benzene by better milling is due to depolymerization. It is recognized that excessive milling, although it increases the solubility of the rubber in benzene, causes a decrease in the mechanical strength of the film thus produced. Dispersion of rubber in tetrachloroethane, trichloroethylene, and carbon tetrachloride, etc., is great, in fact this effect is too great for some practical purposes. Rubber sols in tetrachloroethane and carbon tetrachloride produce a visible precipitate. The prices of trichloroethylene, tetrachloroethane, and carbon tetrachloride are too high.

To sum up the facts above, the rubber solvents for practical purposes should have a uniform solvent power, not leave coarse particles nor too finely dispersed particles and be economical and easy to handle. Carbon disulfide and chloroform have merits as solvents, but carbon disulfide becomes explosive at 150° C. Both carbon disulfide and chloroform are harmful to health, and for these reasons benzene and pure benzene are still in general use. If a solvent such as Scott's solvent ethyl alcohol:chloroform:ethyl ether, in the proportion of 15 : 38 : 47, respectively, or Frankenberg's inflammable solvent—a coal tar naphtha (or with other solvent) is mixed with one part or more of carbon tetrachloride, dichloroethylene, trichloroethylene, tetrachloroethane, or trichlorobenzene, a superior solvent is obtained. From the theoretical point of view, benzene supplemented with carbon tetrachloride, chloroform, or trichloroethylene should give a better result than the use of benzene alone. In practice, however, one should bear in mind that the concentration of rubber is very high, and also that the rubber contains compounding ingredients.

The author wishes to thank Prof. Y. Tanaka, under whose direction these experiments were performed.

Investigations of Colloidal Solutions of Rubber

Part I. The Influence of the Precipitating Agent on Rubber Solutions

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The nature of colloidal solutions of rubber is not yet fully explained in spite of the numerous investigations on the subject which have been carried out. It is well known that the viscosity of these solutions is diminished greatly by heating, by standing, by the action of oxygen and light, and by acids. In the present paper the influence of precipitating agents such as acetone and ethyl alcohol on the change in viscosity of rubber solutions at various temperatures was studied. Smoked sheet was used as the raw material. It was purified from its filtered benzene solution by precipitation once with alcohol and twice with acetone. An Ostwald viscosimeter of brown colored glass with a capillary diameter of 0.7 millimeter and 14.5 centimeters long was used.

TABLE I

	Time in Days	Time of Flow in Minutes			
		Expt. 1	Expt. 2	Expt. 3	Expt. 4
In darkness in brown colored glass flasks	0	191.4	150.0	202.8	171.8
	1	191.4	149.4	202.8	171.6
	2	191.6	149.2	202.8	171.6
	3	171.0	141.0	199.4	166.4
Control, on standing in ordinary glass flasks	2	167.4	135.2	194.2	164.2
	2	158.6	128.2	189.0	161.2

TABLE II

	Relative Viscosity			
	25° C.	40° C.	50° C.	60° C.
Carbon tetrachloride	6.01	5.50	5.20	..
+ acetone 117:18	3.12	2.97	2.83	..
+ alcohol 117:20	1.60	1.58	1.54	..
Gasoline-Benzene
+ acetone	3.61	3.43
+ alcohol	2.60	..	2.47	..
Xylene	4.97	4.83	4.76	4.60
+ acetone	3.62	3.42	3.29	..
+ alcohol 117:13	2.55	2.60	2.61	2.62
Chloroform	4.00	3.84
+ acetone	3.06	2.95	2.85	..
+ alcohol
Benzene
+ acetone	3.32	3.28	..	3.21
+ alcohol	2.73	2.81	..	2.87

First of all, a study was made of the viscosity of the solutions on standing in darkness in brown colored glass flasks. It was found that no change occurred in a short period of two to three days.

The action of precipitating agents was then studied. Purified rubber (0.25 g.) was dissolved in 100 cc. of pure solvent and the solvent and precipitating agent mixed in the ratio of 90:10.

Table II shows that: (1) the addition of the precipitating agent causes a remarkable lowering of the viscosity, as has already been observed, and (2) with the exception of benzene-alcohol and xylene-alcohol solutions the rise in temperature is always accompanied by a lowering of the relative viscosity (time of flow of solution/time of flow of solvent). In order to be certain that in a xylene-alcohol and in a benzene-alcohol solution the increase in the relative viscosity with increase in temperature actually depends on the addition of alcohol, the following experiments were carried out.

Purified rubber (0.25 gram) was dissolved in 100 cc. of pure solvent and 5, 10, 15, and 20 cc. of precipitant were added and the viscosities determined. The results are given in Table III, which shows that, contrary to expectations, in all cases the relative viscosity increased with increase in temperature when the proportions of the mixture reached a definite value.

TABLE III
RELATIVE VISCOSITY OF THE 0.25 PER CENT SOLUTION

	Xylene	Addition of Xylene in Cc.					Addition of Acetone in Cc.					Addition of Alcohol in Cc.			
		5	10	15	20		5	10	15	20		40	5	10	15
25° C.	4.49	4.17	3.87	3.60	3.36	3.76	3.15	2.66	2.99	1.39	2.85	2.41	1.96	1.17	
40° C.	4.32	3.96	3.73	3.46	3.26	3.66	3.10	2.66	2.26	1.43	2.82	2.41	2.06	1.25	
50° C.	4.21	4.08	3.63	3.42	3.19	3.54	3.00	2.59	2.24	1.54	2.79	2.42	2.09	1.26	

TABLE IV
RELATIVE VISCOSITY OF THE 0.25 PER CENT SOLUTION

	Chloroform	Addition of Chloroform in Cc.					Addition of Acetone in Cc.					Addition of Alcohol in Cc.			
		5	10	15	20		25	10	25	40		5	10	15	20
25° C.	3.82	3.53	3.30	3.08	2.88	2.68	3.53	1.71	1.37	2.99	2.63	2.27	1.93	1.56	
40° C.	3.57	3.36	3.16	2.93	2.74	2.57	3.13	1.71	1.39	2.87	2.58	2.23	1.93	1.61	

TABLE V
RELATIVE VISCOSITY OF THE 0.25 PER CENT SOLUTION

	Carbon Tetra- chloride	Addition of Carbon Tetrachloride in Cc.				Addition of Acetone in Cc.					Addition of Alcohol in Cc.		
		10	30	59.4		5	10	20	30		40	2.96	2.60
25° C.	5.16	4.21	3.11	2.01	4.08	3.35	2.43	1.86	1.47	2.96	2.60	2.08	
40° C.	4.73	3.88	2.96	1.09	3.75	3.10	..	1.82	1.48	2.71	3.38	2.00	

Part II. The Effect of the Precipitating Agent and the Influence of the Temperature on the Solvated Particles of Rubber

In Part I it has been shown that the addition of a precipitating agent in excess of a definite proportion to a rubber solution brings about a distinct although small increase in the relative viscosity with increasing temperature. Although a satisfactory explanation of this phenomenon is difficult on account of the complexity of the factors involved, the attempt was made to arrive at a simple explanation in the following way.

In a dilute rubber solution it may be assumed that the particles, regarded statically, are dispersed up to a certain size. It is not unreasonable to suppose that the solvents are immobilized by the process of solvation and that the viscosity changes with the size of the solvated particles. The addition of a precipitant might lower the relative viscosity by exerting a desolvating action on the dissolved particles.

A complete explanation of this action is still impossible, but an idea of it can be obtained from the molar polarity or vectorial sums of the polarity if the increase in the relative viscosity is correlated with the increase in temperature and the change in the former with the proportion of the precipitant.

In rubber solutions, the proportion of precipitating agent necessary to bring about precipitation increases with the temperature.

THE QUANTITY OF PRECIPITATING AGENT (IN CC.) NECESSARY TO BRING ABOUT PRECIPITATION IN 15 CC. OF BENZENE SOLUTION

	Methyl Alcohol	Ethyl Alcohol	Acetone	Butyl Alcohol	Isobutyl Alcohol
25° C.	3.3	4.3	13.2	23.5	21.7
50° C.	4.0	5.1	17.2	27.5	26.1

TABLE VI

		Xylene:Methyl Alcohol			
		100:0	97.2:2.5	95.5	90:10
25° C.	Relative viscosity	4.12	2.89	2.72	2.46
	K	16.3	11.8	10.7	10.7
50° C.	Relative viscosity	3.73	2.81	2.69	2.53
	K	15.6	12.2	11.7	11.0

TABLE VII

		Xylene:Ethyl Alcohol			
		100:0	95:5	90:10	85:15
25° C.	Relative viscosity	4.00	2.82	2.53	2.06
	K	16.4	12.3	11.0	8.5
50° C.	Relative viscosity	3.67	2.37	2.55	2.22
	K	15.4	11.9	11.1	9.4

TABLE VIII

		Xylene:Butyl Alcohol			
		100:0	90:10	80:20	70:30
25° C.	Relative viscosity	4.14	2.79	2.49	1.90
	K	16.8	12.1	10.8	7.6
50° C.	Relative viscosity	3.83	2.73	2.51	2.15
	K	15.9	11.9	10.9	9.0

TABLE IX

		Xylene:Isobutyl Alcohol			
		100:0	90:10	80:20	70:30
25° C.	Relative viscosity	4.14	2.82	2.54	2.18
	K	16.8	12.3	11.0	9.2
50° C.	Relative viscosity	3.83	2.76	2.55	2.27
	K	15.9	12.0	11.1	9.7

The change in the relative viscosity with the temperature is naturally very difficult to follow, because here the solvation process, immobilization phenomenon, and micellar dissociation must be taken into account. In view of the many earlier-known facts and in view of the present experiments, it is believed that with the following assumptions the increase in relative viscosity with increase in temperature can be explained.

1. In dilute solutions the colloid particles of a certain size, regarded statically, are dispersed.

2. After a definite period of time the solution reaches equilibrium, and shows a maximum value which depends upon conditions. This period of time decreases with the temperature.

3. The desolvating effect of the precipitating agent increases with its concentration, but decreases with increase in temperature.

Figure 1 shows the results of the experiments, whereas in Fig. 2 the solvated particles are shown schematically. In Fig. 2 the inner circles represent the size of the solid substance in the solvated particle and the cross-hatched areas the quantity of immobilized solvent.

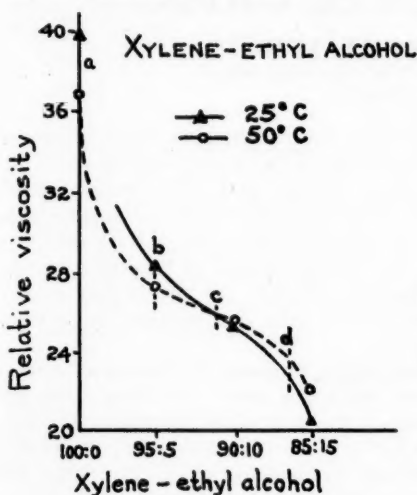


Figure 1

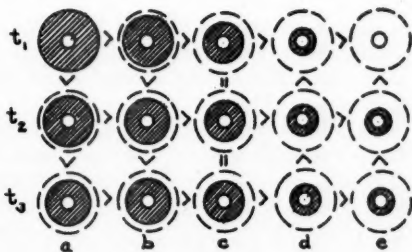


Figure 2

When the temperature is increased above 60° C. a decrease in the rubber micelles or a splitting of the carbon chain takes place, so that in this case a different condition is encountered. Moreover this explanation is not valid for solutions of higher concentration than those employed.

Experimental Part

The purification of rubber and the viscosimetric measurements were carried out as described in Part I.

Twenty-five hundredths gram of rubber was dissolved in 100 cc. solvent or mixture of solvents.

In order to compare the degrees of solvation the Duclaux number K was calculated by the formula:

$$K = \frac{\log \eta}{c} \text{ of the solution}$$

It was observed that the solution of approximately 0.25 per cent concentration conformed very well to the Duclaux formula, so that it may be assumed that solvation was approximately proportional to the K value above.

The Vulcanization of Rubber in Concentrated Solution in the Presence of Ultra-Accelerators

A. Bourbon

The appearance of an article by Thiollet on the formation of jellies in rubber solutions containing rapid accelerators (*Revue Générale du Caoutchouc*, Vol. 9, No. 79, 5-9 (1932); *RUBBER CHEMISTRY & TECHNOLOGY*, 5, 296-300 (1932)) has suggested the publication of the present paper, which deals with experiments in the same field.

In 1927 the author was occupied in studying the vulcanization of thick solutions of rubber containing ultra-accelerators. On account of lack of time this investigation was never carried as far as was desired, therefore the results may appear to be incomplete and the conclusions may seem a little bold because of a certain lack of precision.

The object was to study the rate of vulcanization of these solutions as a function of their concentration. For this reason the effect of a series of solvents under the same conditions was studied, and in this respect the work resembles that of Thiollet. A similar investigation had been made earlier by Boiry (*Caoutchouc & gutta-percha*, 21, 12257-62, 12293-37, 12335-41, 12386-89, 12454-60 (1924); 22, 12507-509 (1925); *India Rubber J.*, 68, 651-54, 687-89, 727-31, 771-73, 807-808 (1924)), but his work was concerned only with dilute solutions, containing at the most 5 grams of rubber for 100 cubic centimeters of toluene. The present work was under different conditions.

EXPERIMENTAL DETAILS

1. Preparation of Solutions

The mixture employed had the same composition as that of Boiry, *i. e.*,

Crepe	100
Sulfur	10
Zinc oxide	2
Accelerator	1

It was mixed on a small laboratory mill under carefully controlled conditions. The mixtures were dissolved as quickly as possible by somewhat crude but sufficiently effective means, and were kept in darkness in a closed cabinet in yellow glass jars having wide mouths. On account of the high concentration, the samples were pastes rather than solutions in the ordinary sense of the word. For this reason it was impossible to follow the course of vulcanization by viscosity measurements, which would have involved difficulties which could not have been overcome with the means at hand. Vulcanization was judged only by the appearance of these solutions—the consistency of the jellies and the content of combined sulfur at the end of a definite time.

2. Determination of Combined Sulfur

The determination of combined sulfur offered some difficulties with such accelerated mixtures. Vulcanization was already in progress at the boiling point of acetone. By extracting the free sulfur directly in the Soxhlet with boiling

acetone there was danger of incorrect results from further vulcanization. This difficulty was overcome by operating in the following manner: The rubber jelly was macerated as finely as possible by passing it once or twice through the rolls of a small mill. It was then extracted for 15 hrs. with cold acetone, which was frequently renewed. After the greater part of the free sulfur was thus removed, extraction by the usual method with boiling acetone was carried out for several hours. The extracted rubber was then dried *in vacuo*, and the combined sulfur determined by the ordinary methods.

DESCRIPTION OF THE EXPERIMENTS

Results

A great many experiments were made, varying:

1. The type of the accelerator
2. The nature of the solvent
3. The proportion of solvent
4. The proportion of accelerator
5. The proportion of sulfur.

The last two series of tests are incomplete and will not be discussed. Only the first three will be described.

1. Influence of the Accelerator

Three accelerators were tested: zinc isopropylxanthate, piperidylpentamethylene dithiocarbamate, and zinc diethyldithiocarbamate. Their activity in solution in the cold decreases in the order given above. The variation in the rate of vulcanization as a function of the proportion of solvent is not the same for the three accelerators. This will be discussed a little later.

2. Influence of the Solvent

The following six solvents were tested: ethylene dichloride, chloroform, toluene, trichloroethylene, carbon tetrachloride, and petroleum benzine (b. p. 70–140°).

The rate of vulcanization in the different solvents varied greatly. It was a maximum with ethylene dichloride and diminished progressively to a minimum with carbon tetrachloride and benzine.

These phenomena, which have been known to rubber technologists for a long time, have received certain practical applications, *e. g.*, in the case of solutions containing ultra-accelerators for cementing inner tubes which would swell too rapidly if made in toluene, but give complete satisfaction with petroleum benzine.

Table I gives some results. The concentration of the solutions was 40 parts rubber to 100 parts solvent. The table shows the approximate time required to form jellies, and in the case of the two first experiments the combined sulfur at the end of 15 and 30 days.

The differences in the rapidity of jelly formation between Experiments 2 and 3 are due to differences in the surrounding temperature. The second series was made in April, 1929 (low temperature), and the third series in June, 1920 (high temperature). These results agree with those of LeBlanc and Kröger with un-accelerated solutions vulcanized with sulfur chloride (*Kolloid-Z.*, 33, September, 1923).

According to these authors, the solvents are classified in the order of their dielectric constants, those with the largest constant having the greatest influence on the swelling of rubber. This was also found in the present work, but for vulcanization rather than for swelling.

No. 1.	Ethylene dichloride	Dielectric constant	10.40
No. 2.	Chloroform	Dielectric constant	5.10
No. 3.	Toluene	Dielectric constant	2.33
No. 4.	Carbon tetrachloride	Dielectric constant	2.25
No. 5.	Heptane (principal component of petroleum benzine)	Dielectric constant	1.90

On the other hand, according to LeBlanc and Kröger, the introduction of sulfur or of halogens into the molecule of solvent brings about more rapid vulcanization of the rubber solution. However, these writers mention two exceptions, chloroform and carbon tetrachloride, in which vulcanization is very slow. Here again the

TABLE I

	Time Required to Form a Jelly	Combined Sulfur at End of		Date of Test
		15 Days	30 Days	
Test No. 1 (Zinc diethyldithio- carbamate)				
Toluene	5 days	...	3.35	July, 1928
Carbon tetrachloride	12 "	...	0.66	
Petroleum benzine	13 "	...	0.37	
Test No. 2 (Piperidylpenta- methylene dithiocarbamate)				
Ethylene dichloride	1 day	4.20	5.30	April, 1929
Toluene	6 days	1.52	3.25	
Carbon tetrachloride	13 "	0.64	1.89	
Petroleum benzine	17 "	Traces	0.50	
Test No. 3 (Zinc isopropylxanthate)				
Ethylene dichloride	12 hours			June, 1930
Chloroform	18 "			
Toluene	24 "			
Trichloroethylene	36 "			
Carbon tetrachloride	72 "			
Petroleum benzine	96 "			
Test No. 4 (Piperidylpenta- methylene dithiocarbamate)				
Ethylene dichloride	1 day			June, 1930
Chloroform	1 "			
Toluene	2 days			
Trichloroethylene	2 "			
Carbon tetrachloride	3 "			
Petroleum benzine	4 "			

results in the present work agree with those of LeBlanc and Kröger. The solutions in trichloroethylene seemed, however, to vulcanize less rapidly than in toluene, but the difference was not very marked. In any case, ethylene dichloride was distinctly in advance of toluene, whereas carbon tetrachloride was distinctly less active.

What conclusions are to be drawn from these results? What does the dielectric constant prove in this case? Is it merely a coincidence? Do these results throw any light on the complex subject of vulcanization? There are so many questions that the incompleteness of our experiments does not make possible a solution.

3. Influence of the Proportion of Solvent

The proportion of solvent was varied from 50 to 300 cc. for 40 grams of rubber. For the different concentrations the rate of vulcanization was determined by the rate of jelly formation and by the determination of combined sulfur.

In Boiry's article already referred to, he says:

"1. The vulcanization of rubber in the solid state in the presence of piperidyl-

pentamethylene dithiocarbamate and zinc oxide is slow but distinct at low temperature.

"2. In the case of vulcanization of rubber in solution the rate is slower and the more dilute the solution, the slower it is. (Stevens has called attention to the same fact for hot vulcanization.) The combined sulfur contents after vulcanization for the same time are lower."

and a little farther on Boiry says:

"7. In rubber in the solid state, the combined sulfur content increases more rapidly than in rubber in solution."

TABLE II
CONTENT OF COMBINED SULFUR

		Solutions: 40 Grams of Rubber per:			
		Dry Mixture	50 Cc.	100 Cc.	150 Cc.
		in %	Toluene	Toluene	Toluene
			in %	in %	in %
1. Solutions in toluene:					
(a) Piperidylpentamethylene dithiocarbamate mixture					
Aged: 4 days		Traces	0.24	0.14	..
14 "		0.15	0.65	0.40	..
19 "		0.18	0.80	0.56	..
31 "		0.20	1.45	1.36	..
		The dry mixture becomes insoluble in toluene at the end of about 25 days	The jellification of these solutions was obtained in 5 and 6 days		
(b) Zinc isopropylxanthate mixture					
Aged: 1 day		Traces	0.35	0.37	..
7 days		0.25	2.66	2.60	..
14 "		0.27	3.82	3.28	..
26 "		0.28	4.70	3.94	..
		The dry mixture becomes insoluble in toluene at the end of about 15 days	The jellification was obtained in 3 days		
(c) Zinc diethyldithiocarbamate mixture					
Aged: 4 days		0.03	0.50	0.44	0.29
14 "		0.07	2.50	1.61	1.23
			The jellification was obtained in 4 days and a half		
2. Solutions in petroleum benzene:					
Piperidylpentamethylenedithiocarbamate mixture					
Aged: 197 days		0.38	0.46	0.44	..

The study of more concentrated solutions shows that this is not always the case: The rate of vulcanization in the cold of a rubber solution containing an ultra-accelerator passes through a maximum at a definite concentration, and this varies with the nature of the accelerator, the nature of the solvent, and probably with other factors besides those which have been studied here.

Table II gives some of the results obtained with the three accelerators in toluene and petroleum benzene. This table shows clearly that the combined sulfur content

of the dry mixture is much less than the combined sulfur contents of concentrated solutions. In petroleum benzine where vulcanization was slower, the difference is less noticeable.

For solutions containing zinc isopropylxanthate it was possible to determine the concentration at which the rate of vulcanization was a maximum. Thus in experiment *b* in Table II, the most concentrated solution became a jelly 24 hours later than the most dilute solution. The maximum must therefore lie between the two (in this experiment it would appear from the combined sulfur values that there had been inversion, since the most concentrated solution was most rapidly vulcanized).

As a result of the numerous experiments carried out, the maximum for these solutions appears to be at a concentration of 40 grams of rubber per 70 cc. of toluene.

Efforts to determine this maximum with piperidylpentamethylene dithiocarbamate and zinc diethyldithiocarbamate were unsuccessful. Since the most concentrated solution vulcanized the most rapidly and the maximum was reached at a very low content of solvent, it was difficult to make a homogeneous paste before the jelly formed.

What is to be concluded from these results? How can they be explained? Disregarding the depolymerizing action of solvents which may play a part in the phenomena, though not the only part, these effects can be explained in the following manner:

The closer together the molecules are, the greater is the rate of vulcanization. This is what led Stevens and Boiry to conclude that the maximum rate was obtained with dry mixtures. The solvent, however, plays the part of a vehicle for the sulfur and the accelerator. As long as the distances between the reacting molecules are not too great, *i. e.*, in a concentrated solution, the solvent by transporting the sulfur and accelerator facilitates their contact with the rubber so that the solution can vulcanize more rapidly than the dry mixture. Therefore, starting with the dry mixture, the rate of vulcanization increases with the percentage of solvent up to the point where, as a result of too great distances between the molecules, it decreases until, for great dilutions, it becomes less than the rate of vulcanization of the dry mixture.

The greater the proportion of accelerator in the solution the more concentrated is the solution with which the maximum rate is found. This is why zinc isopropylxanthate with a very low solubility shows a maximum with a rather high proportion of solvent and which is relatively easy to determine.

Boiry's investigation led him to attempt to explain the process of vulcanization. Do the results obtained with concentrated solutions confirm his view? To a certain degree they do, in spite of the fact that our results differ from his. It seems clear to us, as a result of further evidence which we have obtained, that his hypothesis is correct: In solution vulcanization takes place in two steps: first, combination of sulfur and, secondly, polymerization. However, we would go further than he and say that the same must be true of a dry mixture.

In the course of the experiments, it has been established many times that the dry mixture remains soluble in toluene for about twenty days, but two or three days later, when the combined sulfur content is already appreciable, the same mixture treated for only a few hours with either cold or boiling acetone becomes insoluble. This fact has an important bearing on our determinations of sulfur. Does acetone promote the combination of sulfur? If it does, is this influence greater with the macerated jellies, and is not the combined sulfur found for the jellies in reality too high? This is probably not so, or at least such an effect of

acetone is probably negligible. If a portion of the solution is withdrawn when vulcanization has begun but before a jelly is formed, this paste which disperses very well in toluene becomes insoluble, not only when treated with acetone but also when dried *in vacuo*. Attention has already been called to this phenomenon by several authors, including Bernstein, Stevens, and Boiry. Acetone is therefore primarily only a condensing agent, and its effect on the combination of sulfur with rubber is practically negligible.

The conversion of the dry mixture to the insoluble state by acetone seems to indicate that, in the cold, polymerization does not proceed parallel with vulcanization. As in solution, polymerization is complete only after the combination of sulfur, either spontaneously at the end of a certain time, or under the influence of a condensing agent such as acetone.

The Effect of Simple Carbohydrates on the Vulcanization of Rubber

R. O. Bishop and E. Rhodes

Introduction

In continuation of investigations on the vulcanization effects of *Hevea* lipin (*Quarterly Journal*, Vol. 2, No. 3) the question arose as to the possible influence of the sugar with which lipin is known to be associated. The fact that, in spite of the presence of sugars, the behavior of raw rubber plus lipin on the mixing rolls is apparently similar to that of raw rubber plus lecithin, suggests that the sugars might be without influence.

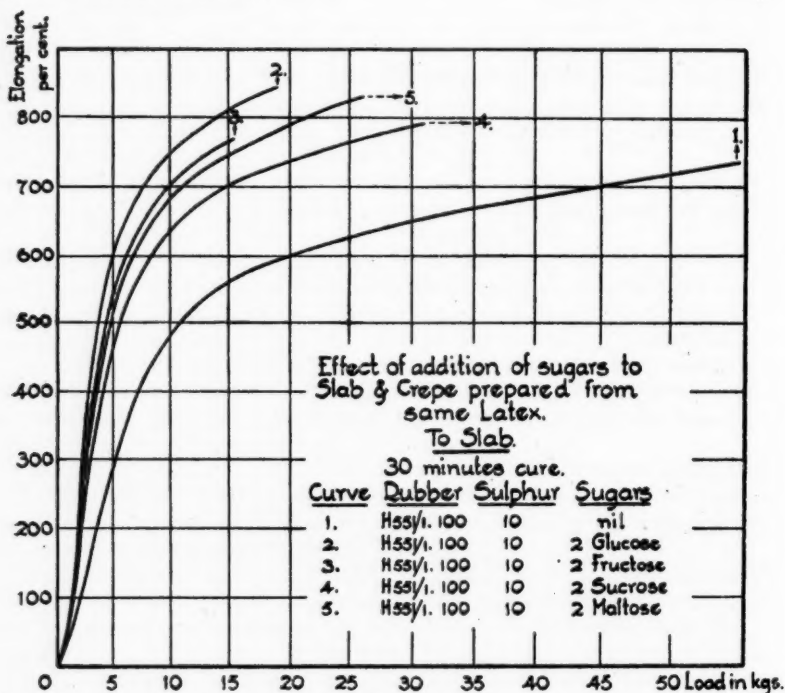


Figure 1

While it is recognized that, for the proper understanding of their influence, it is essential to isolate and characterize the free sugars present in latex, it was considered that the vulcanization effects which we had observed were sufficiently significant in their possible bearing on plantation rubber variation to call for further investigation, and although our subsequent observations cover only a limited field somewhat divergent from the main line of work, it appears that the present results are worth recording.

TABLE I
SHOWING MINUTES OF RETARDATION OR ACCELERATION EFFECTED IN THE VARIOUS CURES

Type of Rubber Slab (H584/1)	Mins. Cure	Glucose, Per Cent			Fructose, Per Cent			Galactose, Per Cent 0.5		Arabinose, Per Cent			Sucrose, Per Cent			Maltose, Per Cent		
		1	2	3	1	2	3	1	2	1	2	3	1	2	3	1	2	3
Slab (H584/1)	45	+5	+7	+10														
	50	+5	+5	+5														
	55	+5	+7	+7														
	60	-10	-10	-15	-7	-10												
	70	-10	-15	-15	-10	-15	-15											
Crepes (H584/2)	20	+20	+20	+20														
	30	+15	+25	+30	+15	+20	+20											
	40	-15	-25		-20	-20												
	50	-15	-20		-20	-20												
	70	-15	-20		-20	-20												
Slab (H551/1)	30	+20	+20	+30														
	40	+20	+20	+30														
	50	+20	+20	+30														
	60	+20	+20	+30														
	70	+20	+20	+30														
Crepes (H551/2)	30	+20	+25															
	40	+20	+25															
	50	+20	+25															
	60	+20	+25															
	70	+20	+25															
Slab (L436)	30	+20	+20	+30														
	40	+20	+20	+30														
	50	+20	+20	+30														
	60	+20	+20	+30														
	70	+20	+20	+30														
Crepes (L335)	30	+20	+25															
	40	+20	+25															
	50	+20	+25															
	60	+20	+25															
	70	+20	+25															
Slab (L455)	30	+20	+25															
	40	+20	+25															
	50	+20	+25															
	60	+20	+25															
	70	+20	+25															
Crepes (L458)	30	+20	+25															
	40	+20	+25															
	50	+20	+25															
	60	+20	+25															
	70	+20	+25															
Slab (A2/2)	30	+20	+25															
	40	+20	+25															
	50	+20	+25															
	60	+20	+25															
	70	+20	+25															
Crepes (A2/1)	30	+20	+25															
	40	+20	+25															
	50	+20	+25															
	60	+20	+25															
	70	+20	+25															

(1) A plus (+) sign represents a retardation of vulcanization and a minus (-) sign an acceleration.
 (2) In general, slab rubbers show a retardation and crepe rubbers an acceleration. The opposite holds in two cases, i. e., slab rubber 455 which is accelerated by 1 per cent of sucrose and crepe rubber 458 which is retarded by 2 per cent of maltose.

In order to investigate this, mixings were made to determine the effect of the simpler carbohydrates in rubber-sulfur vulcanizates, especially since there are records of the presence of carbohydrates occurring free in latex.^{1,2,3,4,5,6,7,8}

At first the work was confined to mixing simple sugars with plantation rubber on warm rolls.

The mixings were made by incorporating 10 grams of sulfur with 100 grams of rubber on rolls at a temperature of about 60° C. The crystalline sugar was added in the required proportion to the plastic mass, and the mixing was completed in the ordinary manner. The amounts of sugar added as percentages on the raw rubber are shown in Table I.

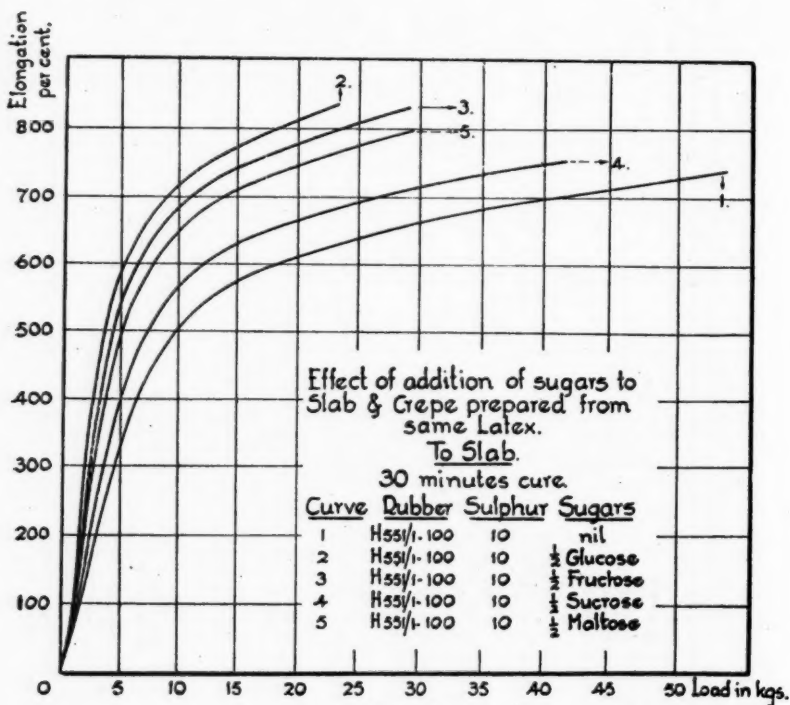


Figure 2

In all cases the mixing proceeded quite normally, and there were no signs of the peculiar effects observed when *Hevea* lipin is incorporated with rubber. The subsequent testing of the vulcanized mixes, however, gave stress-strain curves which did not coincide with the controls. In almost every case there was evidence that the added sugar had affected the rate of vulcanization of the rubber.

Since the results promised to have some significance, further investigations were made. The subsequent observations, although covering only a limited field, appear to be worth recording.

Table I gives the number of minutes of retardation or acceleration of vulcanization produced by various sugars when mixed with simple rubber-sulfur mixes.

The curves shown in the accompanying diagrams were drawn by a Scott machine adapted for ring test-pieces. For purposes of control, a rubber-sulfur mix without sugar was invariably made at the same time as those containing sugars, and test-pieces were cured in the same mold and tested at the same time. For this reason the results recorded for acceleration or retardation produced by the sugar are strictly comparable with those of the control sample. All the results recorded refer to this type of control; for example, the retardation of 10 minutes recorded for the mix, containing 2 per cent sucrose and slab rubber H551/1, was obtained against the control mix of this rubber, mixed, cured, and tested at the same time. Specimen curves are shown in Figs. 1 to 8.

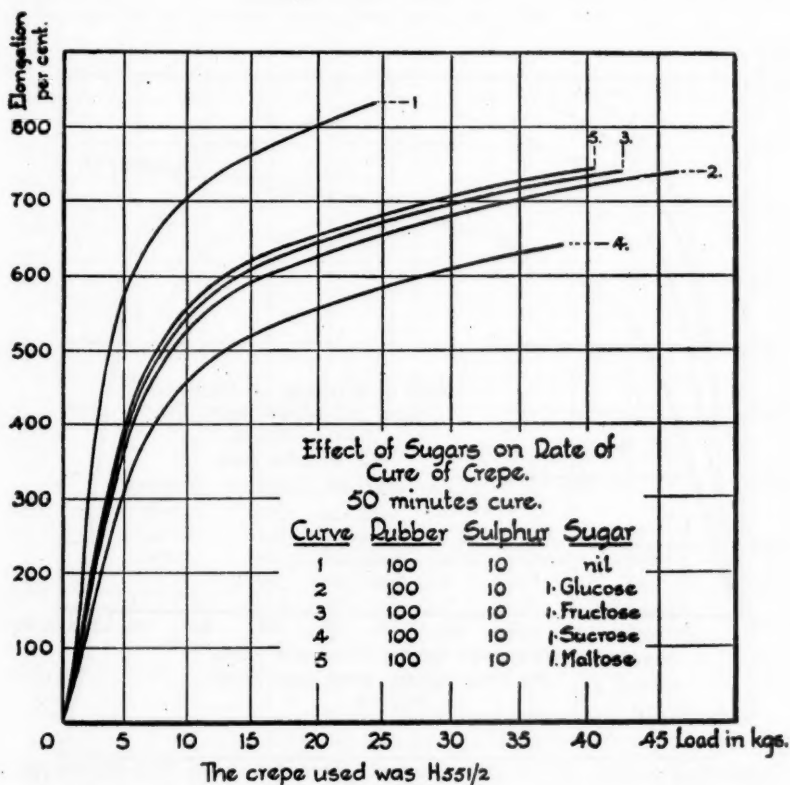


Figure 3

Discussion

From these results it is evident that the rate of cure of a fast-curing rubber (slab rubber) is retarded, while that of a normally slow-curing rubber is accelerated, by the addition of small quantities of sugars. These effects are neither uniform nor proportionate to the quantity of added sugar. The results do not appear to be related to the constitution of the sugar.

Various authors have recorded the presence in *Hevea* latex of true sugars, as well as quebrachitol, and in view of the amounts stated to be dialyzable, it would

appear that these sugars are likely to exert some influence on the vulcanization properties of plantation rubber. The means at our disposal have so far prevented us from confirming the presence of free sugars, but it has been possible to separate quebrachitol by a routine method. Daily supplies of latex from trees of known history have been treated, and the quebrachitol obtained has been bulked and purified. The purity of the preparations has been determined by melting point determinations. The material when pure is white and crystalline, has a melting point of 191°C ., and does not darken in color on storage or melting. In order to ascertain the influence of quebrachitol on vulcanization, mixes of normally fast and slow curing rubbers containing 1, 2, and 3 per cent of quebrachitol were made in the manner described, together with control samples.

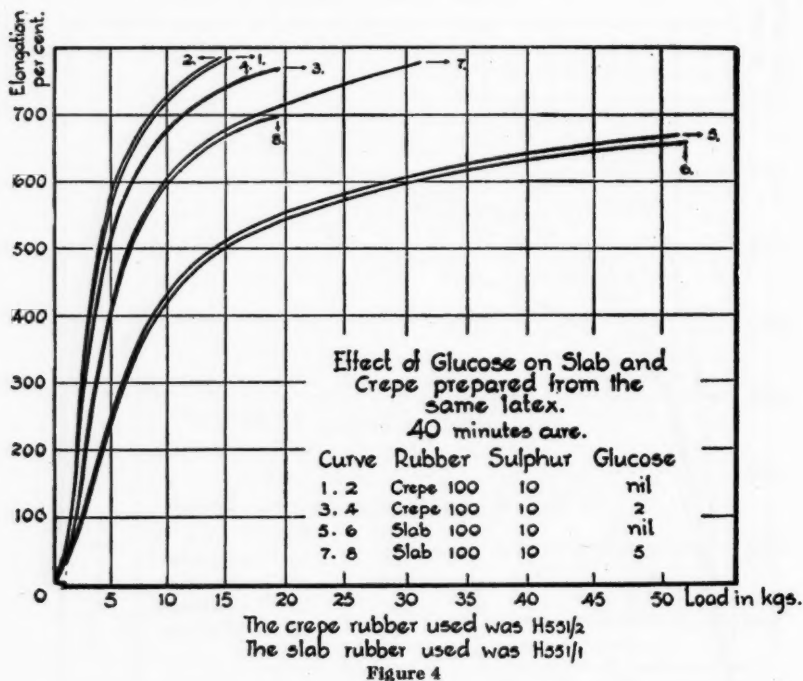


Figure 8 illustrates the results obtained. It will be seen that the results are in complete agreement with those obtained by Stevens⁹ and that the effect of quebrachitol differs essentially from that of the true carbohydrates in that retardation of vulcanization is produced in all types of rubber, and that the effect is approximately proportional to the amount of added quebrachitol.

Having examined the effect of sugars when mixed with dry raw rubber, it was considered advisable to examine rubber prepared from latex to which sugars had been added. For this purpose, aqueous solutions of sugars were mixed with latex immediately before coagulating with acid in the ordinary way. From this latex were prepared both crepe and slab rubber. Control samples of both varieties were prepared from another portion of the same bulked latex to which no sugar had been added. It should be remarked here that, in the earlier work on dry

mixes, the slow and fast curing rubbers were prepared from latices which, although coming from the same field, were not necessarily identical in composition.

In the preparations from the treated and untreated latex of the crepe rubber (samples H584/2, H551/2, and A2/1, Table I) the coagulum was machined into crepe within 24 hours after the collection of the latex. In the case of the corresponding slab rubber, the coagulum was allowed to mature for seven days before machining. The washing, machining, and drying processes were identical.

In every experiment in which sugars were incorporated with latex, the above

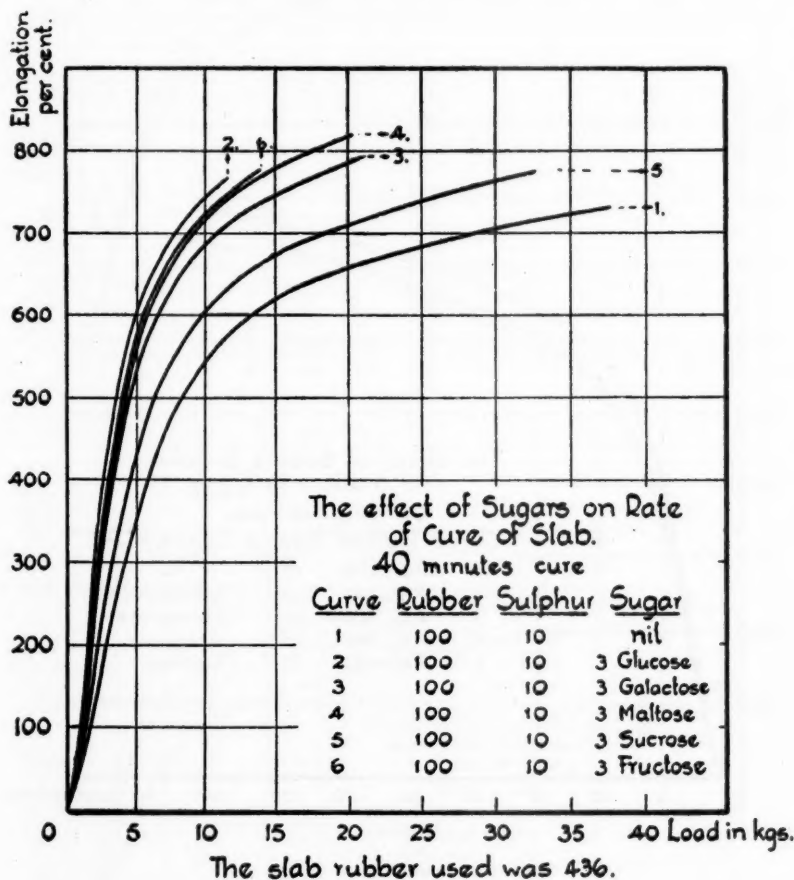


Figure 5

procedure was adopted, and every sample of rubber was compared with a control from a corresponding portion of the same bulked latex. This method was adopted in order to ascertain whether the accelerating or retarding effects of any particular sugar on vulcanization were influenced by the treatment undergone by the coagulum previous to washing and machining. Figures 6 and 7 illustrate the effects produced by the addition to latex of sucrose, dextrose, lactose, and quebrachitol in quantities calculated to give one per cent on the dry rubber content of the latex.

It has been recorded by Gorter² that the dialyzable sugars of latex may amount to 0.25 per cent calculated on the latex.

The results obtained are in agreement with those obtained when sugars are mixed with dry rubber, *viz.*, that acceleration of vulcanization occurs with a slow-curing (crepe) rubber, and retardation of vulcanization with a fast-curing (slab) rubber, when both types are from the same bulked latex. On the other hand, if a fast-curing rubber is prepared by dropping latex into alcohol and rapidly drying the coagulum in thin sheets, the effect of added sugar when mixed with the dry rubber is a definite acceleration in rate of vulcanization.

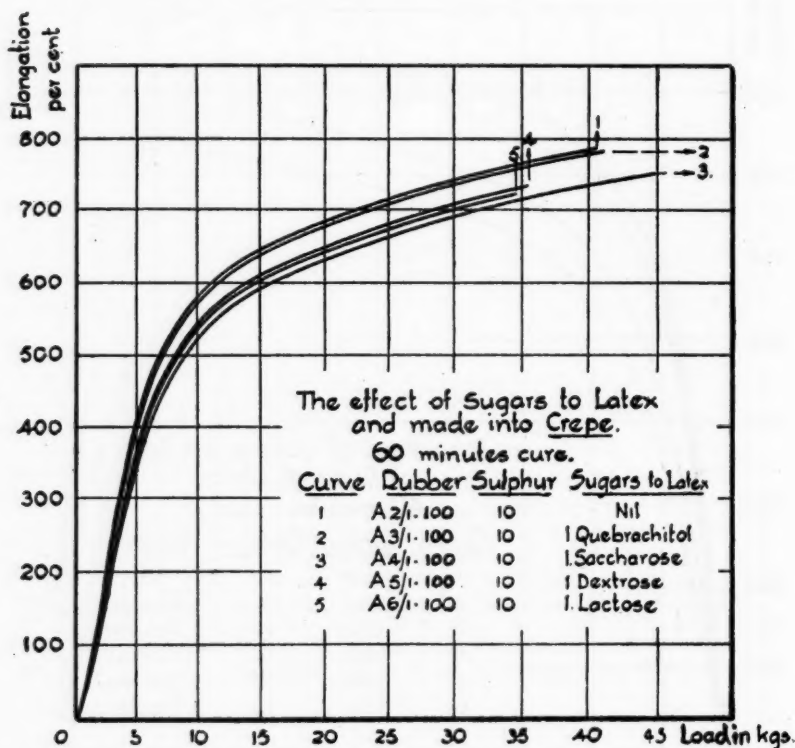


Figure 6

The fact that such comparatively inert, nitrogen-sulfur free substances can exert such opposite effects appears to us to be of some importance. It has been shown that sugars occur naturally in latex and that their proportion may vary with the tree and the season of the year.³ Both these factors may therefore affect the quality of the resulting rubber in a manner depending on the method of preparation. There is, at present, no evidence to show whether the effect of the sugars is achieved directly or through the intermediate action of other substances.

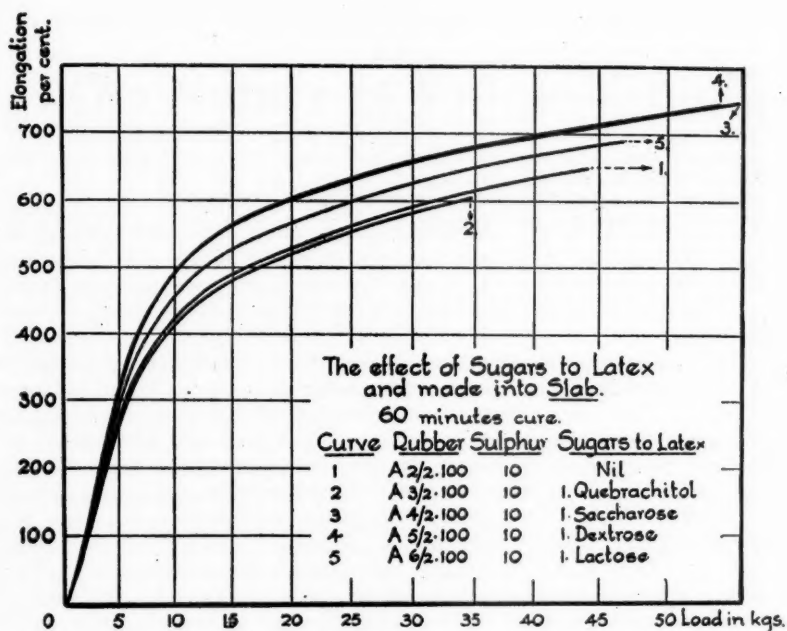


Figure 7

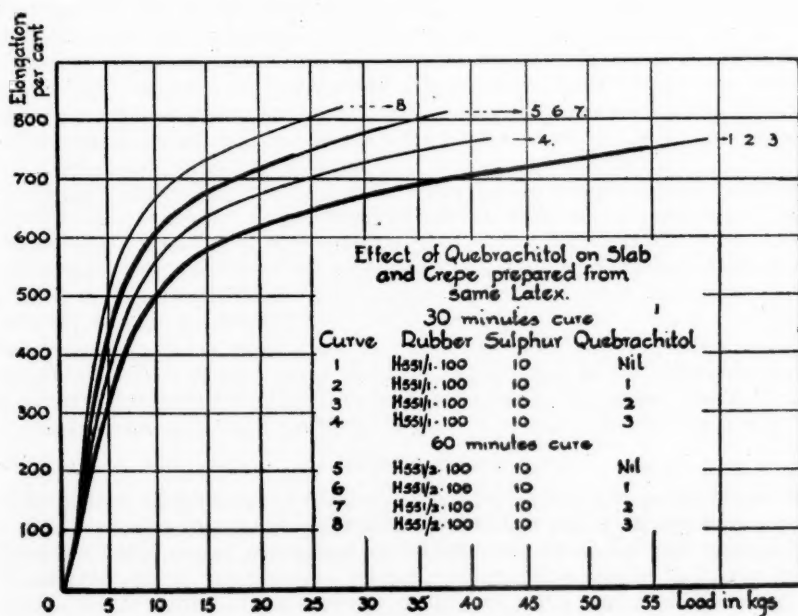


Figure 8

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The Nature of Vulcanization

Part V

H. P. Stevens and W. H. Stevens

In previous communications¹ we have discussed the mechanism of the vulcanization of rubber, and have been led to the conclusion that the improvement in physical properties resulting from this change is due primarily to a reinforcing action of the product of the combination of rubber with the vulcanizing agent.

It is considered essential that the chemical combination between the rubber and the vulcanizing agent should first occur, as no vulcanization effect is otherwise obtainable, and that this combination results in the "colloidal growth" of the reaction product throughout the dispersion medium.

At various times, especially since the advent of accelerators, it has been suggested² that vulcanization may be partly or wholly due to a true polymerization of the rubber molecule, in which process the combination of sulfur or other vulcanizing agent (oxygen or selenium) may be regarded as only incidental. This view receives support from the fact that "Duprene," a synthetic "rubber" developed by the du Pont Co.,³ is polymerized to a "vulcanized" condition by heat alone.

In his Colwyn lecture to the Institution of the Rubber Industry,⁴ Whitby has referred to this aspect of vulcanization, and has drawn interesting conclusions from certain analogous experiments in the vulcanization of oils. Vulcanization accelerators (for example, the dithiocarbamates, substituted guanidines, etc.) are thus regarded as polymerizing agents. Whitby found that if an oil was slightly vulcanized by heating with sulfur, *i. e.*, so that it contained combined sulfur, and all free sulfur was then removed by extraction, the addition of organic accelerators with subsequent reheating improved the physical properties. This effect was attributed to a further "vulcanization" of the oil. It was found that the time of heating required to produce gelling of the oil was considerably reduced in the presence of the organic accelerator, despite the fact that the free sulfur had been removed and therefore no further combination of oil and sulfur could take place. Arguing by analogy, Whitby concluded that in the vulcanization of rubber, organic accelerators function primarily as polymerizing agents, although a preliminary combination of the rubber with sulfur is required to initiate the reaction.

It would appear therefore that, by analogy with oils, organic accelerators should function in the vulcanization of rubber in the presence of combined sulfur, even if free sulfur be absent. Whitby chose oils as the subject of his experiments owing to the insolubility of the vulcanized product and other difficulties when working with rubber. The present paper describes experiments on the vulcanization of rubber in which these difficulties have been more or less surmounted, and the direct action of organic accelerators in the presence of combined sulfur has been studied.

Experimental

The method adopted was as follows: A raw rubber mix containing 10 per cent of sulfur was press-vulcanized in sheets and milled on a pair of differentially geared rollers until thin crepes were obtained. These were extracted with acetone for considerable periods, often after a further milling and recreeping to expose fresh surfaces to the action of the solvent. In this way free sulfur was removed as thoroughly as possible, and for the purpose of the experiment it was assumed

to be completely removed. From our experience of acetone extractions we are satisfied that no significant quantity of free sulfur could have remained in the rubber. In any case, as will be seen later, suitable controls were introduced to check this assumption. The "free sulfur-free" material was then mixed with accelerator and heated again. The products obtained in this way were tested physically against controls, and the results are illustrated autographically. The proportion of free sulfur required to "activate" the organic accelerator was also determined.⁵ The results enabled us to determine and allow for the effect produced by free sulfur and to form an approximate estimate of any vulcanization effect which might have been produced by traces of free sulfur remaining in the extracted vulcanizates.

Some difficulty was experienced in obtaining sufficient material for the revulcanization process following acetone extraction, but by using a larger model of our usual extraction apparatus⁶ sufficient material was obtained for the preparation of test-pieces. Wherever possible exact controls have been made, but the mechanical effects of milling with some of the specimens have been difficult to duplicate. Experiments were first made with sulfur-free accelerators, *e. g.*, diphenylguanidine and *p*-nitrosodimethylaniline, and as these gave no positive results further experiments were made using ultra-accelerators.

Results

The results obtained may thus be summarized (all vulcanizations were made at 142° except where otherwise stated):

Expt. No. 1. Originally vulcanized for 15 min. and acetone-extracted for 20 hours; had combined sulfur 0.50 per cent. Extracted rubber (100) mixed with zinc oxide 4, stearic acid 2½, and diphenylguanidine 1; vulcanized for 15 min. and 45 min. The final vulcanizates showed no "cure" (hand tests).

No. 2. Original mix vulcanized for 30 min.; acetone-extracted 30 hours, and the extracted rubber mix (as No. 1) vulcanized for 30 min. and 90 min. No positive results were obtained (hand tests).

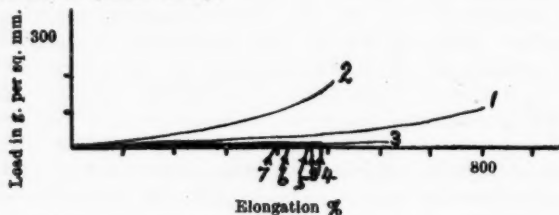


Figure 1

Curve

- 1 10% sulfur mix.
- 2 As above, acetone-extracted, + stearic acid 2.5, zinc oxide 4, zinc diethyldithiocarbamate 1.
- 3 As (1), acetone-extracted, + stearic acid 2.5.
- 4 As (3) + zinc oxide 4.
- 5 As (4) + diphenylguanidine 1.
- 6 As (4) + *p*-nitrosodimethylaniline 1.
- 7 10% sulfur mix not vulcanized but pressed out.
- 8 Rubber (raw) 100, stearic acid 2.5, zinc oxide 4, zinc diethyldithiocarbamate 1.

No. 1 was vulcanized 1 hr. at 40 lb. (steam); nos. 2-8 for 30 min. at 40 lb. (142°) additional cure.

No. 3. Original vulcanization 60 min.; acetone-extracted 24 hours; combined sulfur 0.93 per cent. Mixed as No. 1, but 1 part of zinc diethyldithiocarbamate replaced diphenylguanidine; vulcanized for 30 min. This gave a definite "cure" compared with the controls (see Fig. 1).

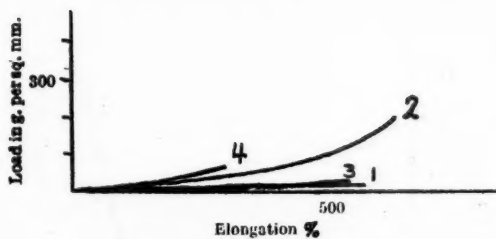


Figure 2

Curve

- 1 Rubber 100, zinc oxide 4, stearic acid 2.5.
 - 2 As (1) + zinc diethyldithiocarbamate 1.
 - 3 As (1) + zinc isopropylxanthate 1.
 - 4 As (1) + benzoyl peroxide 10.
- All mixes vulcanized for 30 min. at 40 lb. (142°).
Rubber used: 10% sulfur vulcanized 1 hr. at 40 lb.;
acetone-extracted.

No. 4. As No. 3, acetone-extracted 36 hours; combined sulfur 0.96 per cent; compounded (as No. 1) with 1 part of *p*-nitrosodimethylaniline or 1 part of diphenylguanidine as accelerator; vulcanized for 30 min. No definite cure was obtained (see Fig. 1). Hand tests placed the diphenylguanidine vulcanizate a trifle firmer than the other, but the testing machine was unable to differentiate between them.

No. 5. As No. 3, acetone-extracted 57 hours. Extracted rubber compounded (as No. 1) with zinc diethyldithiocarbamate 1, zinc isopropylxanthate 1, or benzoyl peroxide 10 as accelerator; vulcanized 30 min. Positive effects were obtained with zinc diethyldithiocarbamate and benzoyl peroxide (see Fig. 2).

No. 6. As No. 3, acetone-extracted 66 hours. Combined sulfur 1.24 per cent. Mixed (as No. 1) with benzoyl peroxide 10 as accelerator; vulcanized 30 min. Result: see Fig. 3. The new rubber control was best. Rubber sulfide was apparently without effect.

No. 7. As No. 3, acetone-extracted 68 hours. Combined sulfur 1.25 per cent. Mixed (as No. 1) with zinc diethyldithiocarbamate 1, tetraethylthiuram disulfide 1, or zinc isopropylxanthate 1 as accelerator; vulcanized for 60 min. at 115°. A definite cure was obtained with zinc diethyldithiocarbamate. The ring broke, but the height of the curve is equivalent to at least 0.5 per cent of free sulfur. A marked result was obtained with tetramethylthiuram disulfide, but no result with zinc isopropylxanthate despite the low temperature of cure (115°). See Fig. 4.

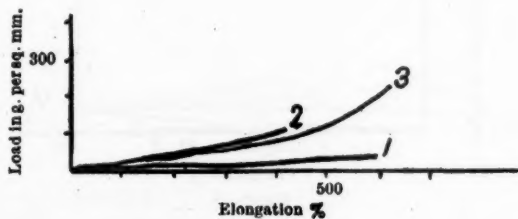


Figure 3

Curve

- 1 Rubber (10% sulfur mix, vulcanized 1 hr. at 40 lb., acetone-extracted) 100, stearic acid 2½, zinc oxide 4.
 - 2 As (1) + benzoyl peroxide 10.
 - 3 Rubber (raw) 100, zinc oxide 4, benzoyl peroxide 10.
- All mixes vulcanized for 30 min. at 40 lb. (steam pressure).

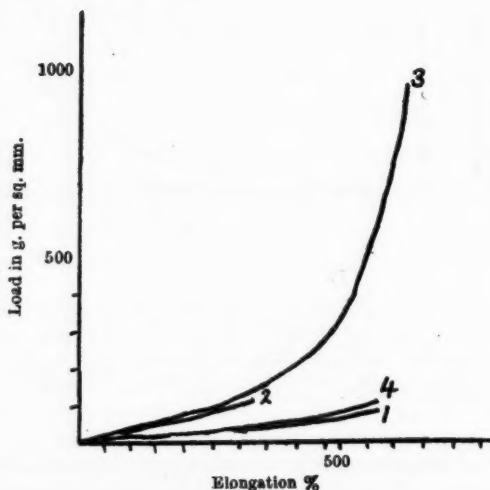


Figure 4

Mix: rubber (10% S mix, vulcanized 1 hr. at 40 lb.; acetone-extracted), 100, zinc oxide 4, stearic acid $2\frac{1}{2}$, accelerator 1. Vulcanized for 1 hr. at 115° .

Curve

- 1 Control (using the extracted rubber).
- 2 Zinc diethyldithiocarbamate.
- 3 Tetraethylthiuram disulfide.
- 4 Zinc isopropylxanthate.

Controls. (To determine the proportion of sulfur required to influence the accelerator: zinc diethyldithiocarbamate.) Milled raw rubber was mixed with 1 part of zinc diethyldithiocarbamate and the following proportions of sulfur: (1) nil, (2) 0.001, (3) 0.01, (4) 0.1, (5) 0.2, (6) 0.5, (7) 0.6, (8) 0.7, (9) 0.8. The samples were vulcanized for 30 min. at 142° and another series for 60 min. at 115° . In the first series of cures, the proportions of sulfur in (1), (2), and (3) gave no result, (4) a slight raising of the curve, (5) twice as marked as (4), (6) much more marked, and so on. Similar results, but all less marked, were obtained for the cures at 115° (see Figs. 5, 6, 7, 8, and 9).

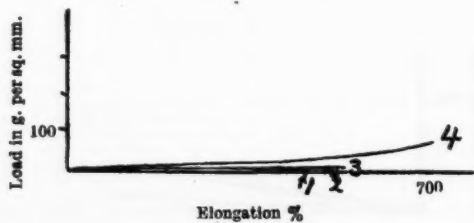


Figure 5

Mix: rubber (raw, milled) 100, zinc oxide 4, stearic acid $2\frac{1}{2}$, zinc diethyldithiocarbamate 1. Vulcanized or 30 min. at 40 lb. (pressure).

Curve

- 1 No sulfur.
- 2 Sulfur 0.001.
- 3 Sulfur 0.0.
- 4 Sulfur 0.1.

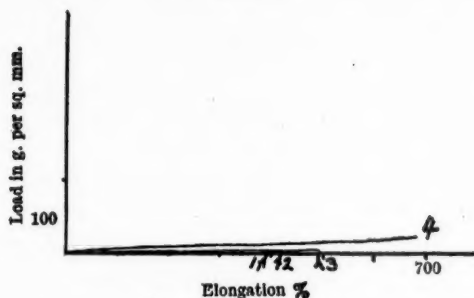


Figure 6

Mix as in Figure 5, but vulcanized for 1 hr. at 10 lb. (pressure).

- Curve
- 1 No sulfur.
 - 2 Sulfur 0.001.
 - 3 Sulfur 0.01.
 - 4 Sulfur 0.1.

It will be seen that in the presence of rubber sulfide positive results were obtained only with zinc diethyldithiocarbamate and tetraethylthiuram disulfide. The activity of the latter is explained by the fact that this accelerator is well known to be unstable and splits off free sulfur during vulcanization. In fact, as is well known, vulcanization can be effected by its means in the absence of added sulfur. The activity of zinc diethyldithiocarbamate, however, cannot be explained in this way, since the control experiments, for instance, curve 8 in Fig. 1, gave no positive effect. Thus, comparing the height of curve 2, Fig. 2, obtained with zinc diethyldithiocarbamate, with that of curve 2, Fig. 8, it will be seen that a "cure" or polymerization equivalent to the presence of 0.6 part of added elemental sulfur has been

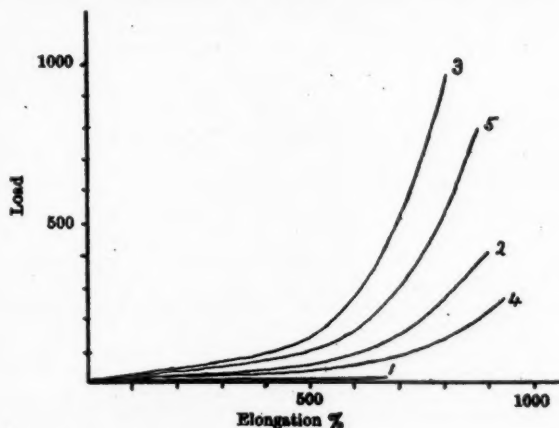


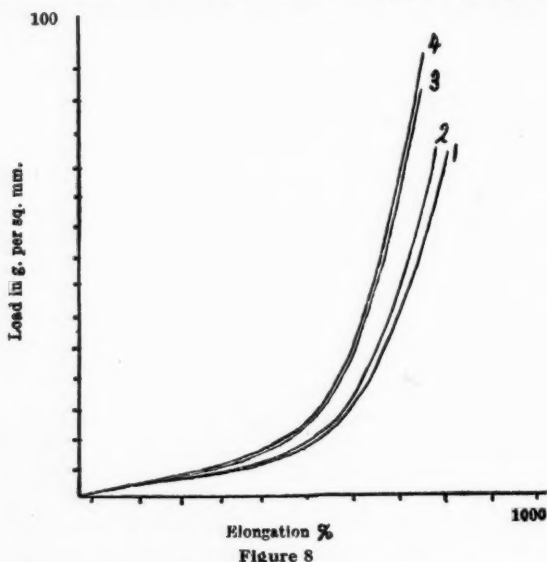
Figure 7

Mix as in Figure 5.

- Curve
- 1 No sulfur.
 - 2 Sulfur 0.2.
 - 3 Sulfur 0.5.
- Vulcanized for 1 hr. at 10 lb. (steam pressure).
- 4 Sulfur 0.2.
 - 5 Sulfur 0.5.
- Vulcanized for 30 min. at 40 lb. (steam pressure).

obtained similarly, curve 2, Fig. 1, shows a cure equivalent to 0.8 part of sulfur. It should be noted that the early termination of curves with the re-cured samples is almost certainly due to the "disaggregation" or mechanical effect of the acetone extractions, crepeing, mixing, etc. In considering the state of "cure" reliance should be placed principally on the position of the curve relative to the horizontal axis.

Reference may also be made to benzoyl peroxide which, according to Whitby, is an active polymerizing agent. That the latter is without effect will be seen from Fig. 3, where the height of curve 2 is almost exactly that of the control, curve 3 plus curve 1, which represents the physical result from the first vulcanization. The presence of rubber sulfide is therefore without effect, and does not produce polym-



Mix as for Figure 5, vulcanized for 30 min. at 40 lb. (pressure).

Curve	
1	Sulfur 0.5.
2	Sulfur 0.6.
3	Sulfur 0.7.
4	Sulfur 0.8.

erization with this reagent. Zinc isopropylxanthate, which is well known to be very active at low temperatures, is also totally without effect despite the inclusion of a low-temperature revulcanization in the series in order to avoid prematurely destroying its activity.

The exceptional behavior of zinc diethyldithiocarbamate is difficult to explain except on the basis of Whitby's theory that it engenders a true polymerization of the rubber in the presence of a small proportion of rubber sulfide. If that is the case, however, why should not the other accelerators examined show a similar effect, however small? As will be shown piperidine 1-carbothionolate does in fact have a similar action but in a modified degree. Of all the accelerators examined, these two alone have given positive results.

To pursue the matter further, experiments were made with various accelerators in which the influence of other organic sulfides on polymerization in a rubber medium was examined. Thus, vulcanized oil, freed from "free sulfur" and other

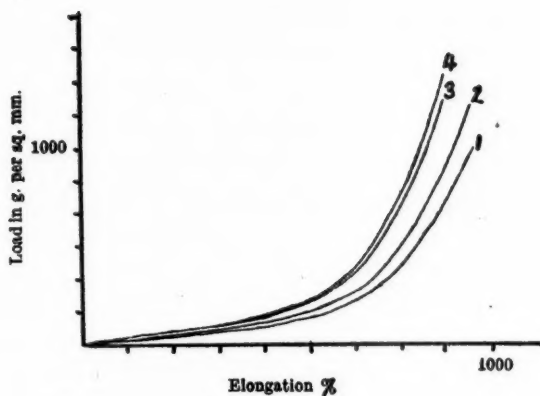


Figure 9

Mix as for Figure 5, vulcanized for 1 hr. at 10 lb. (pressure).

Curve

1 Sulfur 0.5.

2 Sulfur 0.6.

3 Sulfur 0.7.

4 Sulfur 0.8.

(Compare curve 4 with zinc diethyldithiocarbamate curve, Figure 4. The zinc diethyldithiocarbamate curve is equivalent to the 0.8 part of sulfur curve.)

acetone-soluble material, might be expected to behave as a mild polymerizing agent analogous to rubber sulfide. Also two accelerators in conjunction might give an autopolymerizing effect.

The following combinations were first tested: zinc diethyldithiocarbamate, tetraethylthiuram disulfide, and zinc isopropylxanthate, singly, and the first two in combination. Figure 10 shows that in the absence of sulfur and when vulcanizing at a temperature lower than the decomposition temperature of tetraethylthiuram disulfide the accelerators are without autopolymerizing effect. A duplicate test gave similar results, the curve never rising above the elongation axis. Thus, tetraethylthiuram disulfide cannot duplicate the part played by rubber sulfide in activating zinc diethyldithiocarbamate.

The results of experiments with acetone-extracted vulcanized rubber, acetone- and ether-extracted vulcanized oil (substitute), and various accelerators are as follows (see also Fig. 11):

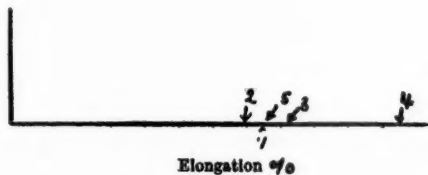


Figure 10

Mix: rubber (well milled) 100, zinc oxide 4, stearic acid $2\frac{1}{2}$, accelerator 1, vulcanized for 1 hr. at 10 lb. (pressure).

Curve

1 Control.

2 Zinc diethyldithiocarbamate.

3 Tetraethylthiuram disulfide.

4 Zinc isopropylxanthate.

5 $\frac{1}{2}$ Zinc diethyldithiocarbamate + $\frac{1}{2}$ tetraethylthiuram disulfide.

Expt. No. 8. A 10 per cent sulfur mix, vulcanized for 1 hour at 142°, acetone-extracted for 92 hours, had combined sulfur 0.98 per cent. Extracted rubber samples were compounded as in Expt. 1, each with 1 part of the accelerators mentioned. Samples vulcanized for 30 min. at 142° gave marked results with all the accelerators in the following order: tetramethylthiuram disulfide, tetraethylthiuram disulfide, zinc diethyldithiocarbamate, piperidine 1-carbothionolate (see Fig. 11).

No. 9. Milled raw rubber mixed as No. 1, but with accelerators as No. 8, in some cases mixed together in equal proportions, i. e., zinc diethyldithiocarbamate,

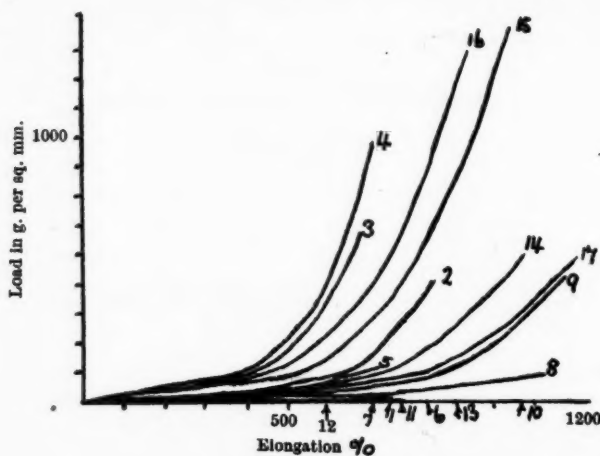


Figure 11

Mix: Rubber 100, zinc oxide 4, stearic acid 2½, accelerator 1, vulcanized for 30 min. at 40 lb. (pressure).

Rubber Used	Curve	Index of Vulcanization Load at 650% Elongation
10% sulfur; vul- canized for 1 hr. at 40 lb. Acetone-ex- tracted	1 No accelerator	1.5
	2 Zinc diethyldithiocarbamate	10.5
	3 Tetraethylthiuram disulfide	48.0
	4 Tetramethylthiuram disulfide	59.0
	5 Piperidine 1-carbothionolate	9.0
Well milled raw rubber	6 No accelerator	0.0
	7 Zinc diethyldithiocarbamate	0.0
	8 Tetraethylthiuram disulfide	2.5
	9 Tetramethylthiuram disulfide	5.0
	10 Piperidine 1-carbothionolate	0.0
Well milled raw rubber. Ex- tracted "sub- stitute" 5 parts	11 Zinc diethyldithiocarbamate tetraethylthiuram disulfide	1.0
	12 Zinc diethyldithiocarbamate piperidine 1-carbothionolate	0.0
	13 No accelerator	0.0
	14 Zinc diethyldithiocarbamate	8.0
	15 Tetraethylthiuram disulfide	21.0
	16 Tetramethylthiuram disulfide	29.5
	17 Piperidine 1-carbothionolate	6.0

tetraethylthiuram disulfide, tetramethylthiuram disulfide, piperidine 1-carbothionolate 1 part each, and zinc diethyldithiocarbamate + tetraethylthiuram disulfide ½ part each, zinc diethyldithiocarbamate + piperidine 1-carbothionolate ½ part each. Vulcanized for 30 min. at 142°. Faint positive results were obtained in the following order: tetramethylthiuram disulfide, tetraethylthiuram disulfide, zinc diethyldithiocarbamate ½ + tetraethylthiuram disulfide ½ (see Fig. 11). Similar but less marked results were obtained when vulcanizing for 60 min. at 115°.

No. 10. Brown rubber substitute was acetone-extracted for 60 hours and ether-extracted for 24 hours. Combined sulfur 16.9 per cent. It was mixed (5 parts) into milled raw rubber (100) with accelerator 1 part (accelerators, etc., as in No. 8). Vulcanized for 30 min. at 142°. A similar series of results were obtained as in Expt. 8, but rather less marked. The order of accelerators was the same. Similar but less marked results were obtained when vulcanized for 60 min. at 115°.

As already explained, the vulcanization effect obtained with tetramethyl- and tetraethylthiuram disulfides is due to the liberation of free sulfur which occurs when vulcanizing with these accelerators. This is shown by the fact that the plain rubber controls show a definite vulcanization effect and the relative order of the two accelerators, the tetramethyl compound being the more active, is the same as that known in commercial practice. The combination of zinc diethyldithiocarbamate and tetraethylthiuram disulfide is also in the position expected from the activity of the reduced proportion of the latter accelerator (curve 11, Fig. 11). In each series of experiments (Nos. 8, 9, and 10) the order of activity of the accelerators is the same, but only in the presence of vulcanized oil or rubber sulfide do the non-free-sulfur-splitting accelerators, *e. g.*, zinc diethyldithiocarbamate and piperidine 1-carbothionolate, show a positive effect and then always in the same order. Since the accelerators in each group are the same, and it is the behavior of the organic sulfide which varies, it would appear that it is the accelerator which has a direct polymerizing effect on the rubber, but that this has to be initiated or catalyzed by the organic sulfide. The fact that sulfur-free vulcanized oil can replace sulfur-free vulcanized rubber in this role confirms this view, and further shows that the normal well-known retarding effect that rubber substitutes have on vulcanization is due to the presence of unvulcanized and/or acidic components, as indeed has long been suspected to be the case.

The fact that the vulcanization effects obtained in Expt. 10 in the presence of purified substitute are greater than those obtained in Expt. 9 in plain rubber mixes may indicate an avenue of investigation profitable to the rubber substitute manufacturing industry.

The broad results of the last series of these experiments are therefore to show that ultra-accelerators have a definite polymerizing effect on raw rubber which is initiated or catalyzed by the presence of certain organic sulfides, particularly, as would be expected, by rubber sulfide. This may be replaced by vulcanized oil, but not by another accelerator; thus the accelerators are not autogenous in their action, and are without effect on themselves.

With regard to the determination of the smallest quantity of sulfur required to "activate" zinc diethyldithiocarbamate, as will be seen from Figs. 5 and 6, we obtained the first positive effect with 0.1 part of sulfur, which agrees well with Bruni's recently published figure of 0.15 per cent.⁷

Conclusions

(1) Diphenylguanidine, *p*-nitrosodimethylaniline, zinc isopropylxanthate, and benzoyl peroxide do not effect polymerization (vulcanization) of sulfur-free rubber in the presence of a small proportion of rubber sulfide.

(2) In the presence of rubber sulfide, zinc diethyldithiocarbamate has a definite vulcanizing effect on rubber containing 1 per cent of combined sulfur. This effect is equivalent in magnitude to that produced by the presence of at least 0.5 per cent of free sulfur in the mixing, a much larger amount than could possibly have remained after exhaustive acetone extraction. The accelerator piperidine 1-carbothionolate has a similar but weaker effect.

(3) The fact that a similar but lesser polymerization is induced by purified vulcanized oil, analogous to the "activation" of the accelerators by rubber sulfide and that the activities of the accelerators are in the same order in both cases, would indicate that vulcanization promoted by accelerators is partly a polymerization activated by the vulcanizing agent and its reaction product with the rubber medium.

(4) It has been found that the smallest proportion of free sulfur to give a measurable vulcanizing effect in the presence of zinc diethyldithiocarbamate is of the order of 0.1 per cent.

References

¹ H. P. Stevens, *J. Soc. Chem. Ind.*, **38**, 192T (1919); **47**, 37T (1928). H. P. Stevens and W. H. Stevens, *Ibid.*, **48**, 55T (1929); **50**, 397T (1931).

² Cf. Whitby, *Trans. Inst. Rubber Industry*, **6**, 59 (1930). Whitby and Simmons, *Ind. Eng. Chem.*, **17**, 931 (1925). Schidrowitz, *India-Rubber J.*, **64**, 802 (1927). Twiss, *J. Soc. Chem. Ind.*, **44**, 106T (1925).

³ *J. Am. Chem. Soc.*, **53**, 4197, 4203 (1931).

⁴ *Trans. Inst. Rubber Industry*, **6**, 60 (1930).

⁵ See also Bruni, cf. *India-Rubber J.*, **51**, 841 (1931).

⁶ *Analyst*, **38**, 143 (1913); **56**, 528 (1931). Cf. the apparatus used by Whitby for determining the acid value of rubber by extracting 30 g. at a time, *Rubber Age* (London), Oct., 1924.

⁷ *Loc. cit.*

Studies on the Aging of Vulcanized Rubber

XI. Consideration of the Influence of Free Sulfur on Aging of Vulcanized Rubber

T. Yamazaki and K. Okumura

Although it has been generally known that free sulfur in a vulcanized rubber is likely to change into sulfuric acid during aging, the authors pointed out in their Ninth Report that a part of the combined sulfur also decomposes during aging, with the formation of sulfuric acid. Therefore the authors in this report proceeded to find the relation between the proportions of free sulfur in vulcanized rubber at the state of optimum cure and its aging. The samples used for these experiments were as follows:

	Sample No.	Composition				Time of Optimum Cure (Min.)	Original Tensile Strength (Kg./Sq. Mm.)	Free Sulfur (%)
		Rubber	Sulfur	Diphenylguanidine	Zinc Oxide			
Diphenylguanidine	50	50	2.5	0.1	47.4	70	1.66	1.02
Diphenylguanidine	51	50	2.5	0.3	47.2	33	1.87	1.36
Diphenylguanidine	52	50	2.5	0.6	46.9	15	2.07	1.65
Diphenylguanidine	54	50	2.0	0.1	47.9	80	1.46	0.59
Diphenylguanidine	55	50	2.0	0.3	47.7	55	1.86	0.59
Diphenylguanidine	56	50	2.0	0.6	47.4	25	2.07	0.60
Diphenylguanidine	57	50	2.0	1.2	46.8	15	2.16	0.66
Diphenylguanidine	58	50	1.5	0.1	48.4	90	1.39	0.45
Diphenylguanidine	59	50	1.5	0.3	48.2	55	1.74	0.49
Diphenylguanidine	60	50	1.5	0.6	47.9	30	1.95	0.49
Diphenylguanidine	61	50	1.5	1.2	47.3	15	2.15	0.55
Diphenylguanidine	62	50	1.0	0.1	48.9	90	1.17	0.26
Diphenylguanidine	63	50	1.0	0.3	48.7	70	1.59	0.26
Diphenylguanidine	64	50	1.0	0.6	48.4	35	1.94	0.25
Diphenylguanidine	65	50	1.0	1.2	47.8	20	2.10	0.26

	Sample No.	Composition				Time of Optimum Cure (Min.)	Original Tensile Strength (Kg./Sq. Mm.)	Free Sulfur (%)
		Rubber	Sulfur	Di-o-tolylguanidine	Zinc Oxide			
Di-o-tolylguanidine	50	50	2	0.1	47.9	50	1.59	0.92
Di-o-tolylguanidine	51	50	2	0.3	47.7	30	1.81	0.96
Di-o-tolylguanidine	52	50	2	0.6	47.4	15	1.98	1.11
Di-o-tolylguanidine	53	50	2	1.2	46.8	5	2.19	1.13
Di-o-tolylguanidine	54	50	1.5	0.1	48.4	70	1.58	0.48
Di-o-tolylguanidine	55	50	1.5	0.3	48.2	35	1.83	0.56
Di-o-tolylguanidine	56	50	1.5	0.6	47.9	18	1.93	0.56
Di-o-tolylguanidine	57	50	1.5	1.2	47.3	6	2.19	0.58
Di-o-tolylguanidine	58	50	1	0.1	48.9	80	1.33	0.33
Di-o-tolylguanidine	59	50	1	0.3	48.7	50	1.70	0.31
Di-o-tolylguanidine	60	50	1	0.6	48.4	25	1.88	0.33
Di-o-tolylguanidine	61	50	1	1.2	47.8	7	2.06	0.33

All these stocks were vulcanized to the state of optimum cure, determined from tensile product time of cure curves, in order to obtain comparable conditions of vulcanization.

All these samples were aged in a Geer oven at a temperature to $70^{\circ} \pm 1^{\circ} \text{C.}$ for 50 to 500 hours, and at intervals the mechanical strength and the proportions of free sulfur of the aged samples were determined.

From the results of these determinations it was confirmed that the proportion of free sulfur in the vulcanized rubber is not a reliable means of predicting the aging properties of vulcanized rubber; and it was also found that proper sulfur-accelerator combinations, as well as shortening of the time of cure, are far more important from the viewpoint of aging.

Studies on the Combined Use of Two Different Accelerators

I. Diphenylguanidine and Mercaptobenzothiazole

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Numerous new accelerators appeared in the market after the rapid development of the rubber industry. Although the use of most of these accelerators alone gives sufficient accelerating action, in some cases it is accompanied by scorching from rapid vulcanization. When one accelerator is combined with another suitable one, such damage can be prevented or reduced.

This problem has been studied by Thiollet and Martin (*Caoutchouc & gutta-percha*, 26, 14494). They called attention to the fact that by a proper combination of one or more of the accelerators: zinc ethylphenyldithiocarbamate, mercaptobenzothiazole, ethyldineaniline, diphenylguanidine, anhydroformaldehydeaniline, etc., a much different result was obtained. Norris (*India Rubber World*, 82, 53-55) describes various combinations of different commercial accelerators by using the ingredients in different ratios. The desirable combinations were deduced from the tendency to scorch during vulcanization at 220° F. The substances used in this experiment were commercial products of unknown purity, and the combination of these ingredients was not based on their chemical structure. Emden (*Kautschuk*, 6, 137) stated that a combination of accelerators increased their activity because of a lowering of the melting point. There are no investigations in regard to the determination of the eutectic curves of the different accelerators. Therefore the authors tried the use of different commercial organic accelerators based on the eutectic curves, as in the case of metallurgy.

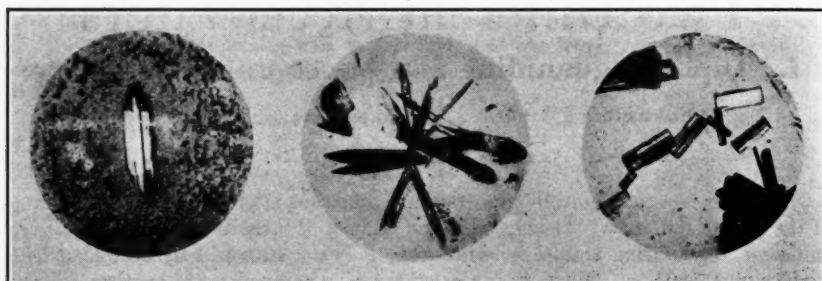
Studies of a eutectic curve indicate whether or not there is any molecular combination. If there is such chemical combination, the eutectic point is estimated, rubber is compounded with the ratio of accelerators found at this point, and the effect of vulcanization is studied. The authors first studied the combined use of two well-known accelerators, viz., mercaptobenzothiazole and diphenylguanidine. Further work on other accelerators is in progress.

Experimental Procedure

(a) *Determination of the Eutectic Curve.*—The methods of determining the eutectic curves of the different organic compounds, as in the case of metallic alloys, are based on the work of Rheinboldt (*Z. prakt. Chem.* (2), 111, 242; 112, 187; 113, 199) and Asahina (*J. Chem. Soc. Japan*, 51, 10, 662-668).

The materials under observation, when too finely ground, became colored when melted, because of partial decomposition, and this coloration obscured the observation. Therefore the samples were pulverized in a mortar and, without further mixing, were placed in a 0.05-mm. capillary tube to a height of 5 millimeters. The melting point was determined as usual by raising the temperature one degree per min. until the sample started to melt. The softening point and the point of complete melting were recorded. Diphenylguanidine was purified by the method of Carlton (*J. Am. Chem. Soc.*, 44, 1464-1478), i. e., the material previously dried over

calcium chloride was dissolved in hot toluene, was cooled to crystallize, and was filtered. This process was repeated three times. The melting point was 148° C. Mercaptobenzothiazole was purified from hot benzene as above. The melting point was 178° C.



Mercaptobenzothiazole

Diphenylguanidine

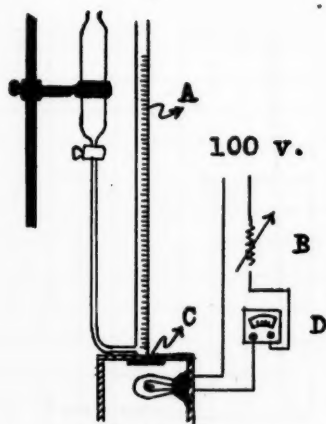
Molecular compound

The material thus obtained was used in determining the eutectic curve. The softening point and the melting point of the diphenylguanidine and of mercaptobenzothiazole mixture are shown in Table I and Fig. 1. The results show two eutectic points, one at 129° C. (mercaptobenzothiazole 8.5 per cent, diphenylguanidine 91.5 per cent) and one at 145° C. (mercaptobenzothiazole 57.5 per cent, diphenylguanidine 42.5 per cent). Diphenylguanidine and mercaptobenzothiazole form a molecular compound at 55.94°, with the molecular ratio of 1:1. Therefore these accelerators combined in this ratio were studied in regard to scorching.

TABLE I

Per Cent by Weight Mercapto- benzothiazole	Diphenyl- guanidine	Softening Point	Melting Point
2.72	97.28	130.0	144.5
5.01	94.99	129.0	143.0
10.55	89.45	129.5	140.0
12.39	87.61	129.0	149.0
23.44	76.56	130.0	163.0
35.46	64.54	129.0	169.0
44.06	55.94	155.0	170.0
50.00	50.00	146.0	167.3
55.30	44.70	144.0	160.0
62.65	37.35	144.0	161.0
75.00	25.00	146.0	174.0
85.60	14.40	146.0	177.0

(b) *Test of Scorching.*—The scorching test was a slight modification of the method of Toyabe and his co-workers (*J. Soc. Chem. Ind. Japan*, 32, 1104–1107) and that of Thies (*Ind. Eng. Chem.*, 20, 1223). The compoundings of the samples are shown in Table II. The proportions of accelerators were equal in all cases. Sample B consisted of the mixture found at eutectic point E_1 in Fig. 1, sample C was the mixture which formed the molecular compound at M in Fig. 1, and sample D was the eutectic mixture E_2 in Fig. 1. Seven hundred and fifty grams of rubber were milled for fifteen minutes on a 6" × 12" roll mill, and then zinc oxide and sulfur were added and mixed. The batch was divided into five equal portions, and the accelerators were added in accordance with the compounding in Table II. The product was pressed to a layer 0.13 cm. thick and let stand for 24 hours, after which it was cut into round discs 1.6 cm. in diameter. These were placed in large



Turbidimeter
 A. Graduated cylinder
 B. Rheostat
 C. Cobalt glass
 D. Ammeter

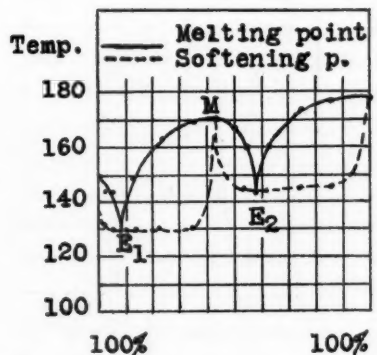


Figure 1

test tubes and vulcanized at 70° and at 100° in an oil bath for a definite length of time, depending on the test. Vulcanized samples thus prepared were placed in large test tubes (3 × 15 cm.) containing 50 cc. of gasoline, stoppered, and shaken 100 times per minute. The gasoline was then poured into a Vogt turbidimeter (*India Rubber World*, 65, 347). The turbidity was estimated by pouring the

TABLE II

Sample	Smoked Sheet	Zinc Oxide	Sulfur	Diphenyl-guanidine	Mercapto-benzothiazole
A	100	10	5	1.000	0.000
B	100	10	5	0.915	0.085
C	100	10	5	0.558	0.575
D	100	10	5	0.425	0.575
E	100	10	5	0.000	1.000

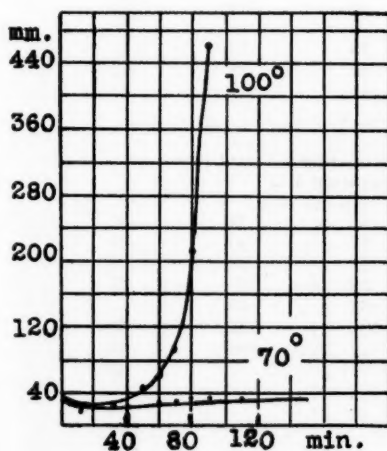


Figure 2—Sample A

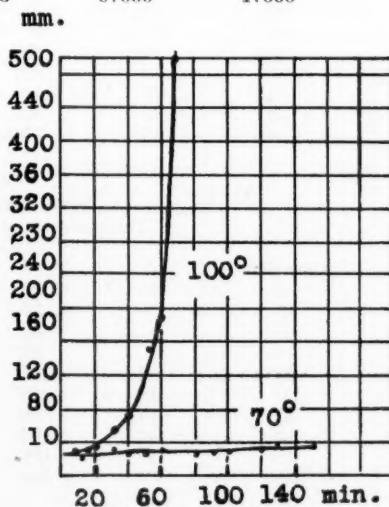


Figure 3—Sample B

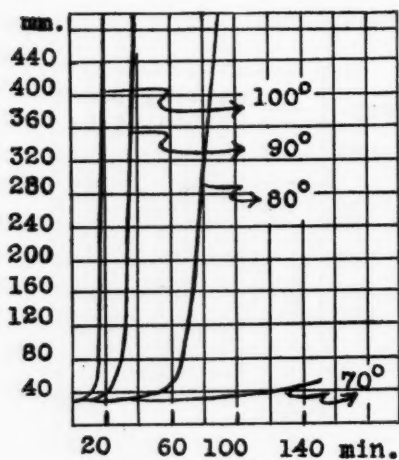


Figure 4—Sample C

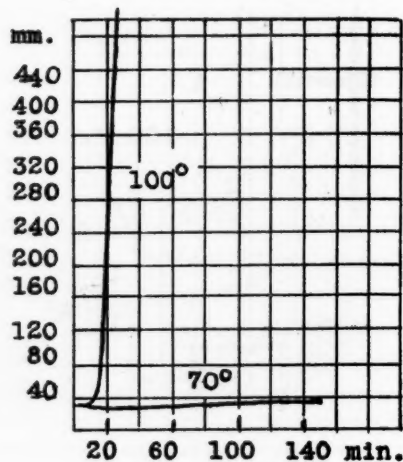


Figure 5—Sample D

TABLE III
RECIPROCAL TURBIDITY OF VULCANIZED SAMPLES
Temperature of Vulcanization 70°

Time (Min.)	Reciprocal Turbidity (Mm.)				
	A	B	C	D	E
0	29	26	27	29	34
10	24	24	25	23	31
20	24	25	25	23	31
30	25	30	27	28	..
40	24	26	28	29	..
50	28	24	24	25	31
60	29	25	28	28	29
70	29	..	25	29	28
80	32	25	27	29	31
80	32	25	27	27	29
90	33	28	30	33	30
100	25	27	29	33	29
110	33	30	28	29	31
120	32	30	30	34	30
130	33	31	35	29	29
140	30	32	43	36	32
150	30	35	44	34	32

TABLE IV
RECIPROCAL TURBIDITY OF VULCANIZED SAMPLES
Temperature of Vulcanization 100°

Time (Min.)	Reciprocal Turbidity (Mm.)				
	A	B	C	D	E
0	30	26	27	80	31
5	..	26	22	28	..
10	50	30	32	30	27
15	..	30	62	49	..
20	30	34	500	332	29
30	28	48	..	500	34
40	30	66	32
50	50	154	40
60	60	196	73
70	73	500	132
80	212	500
90	467

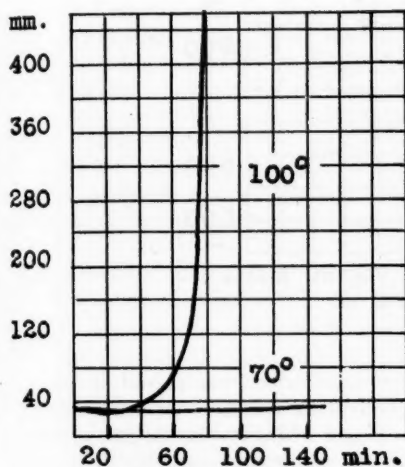


Figure 6—Sample E

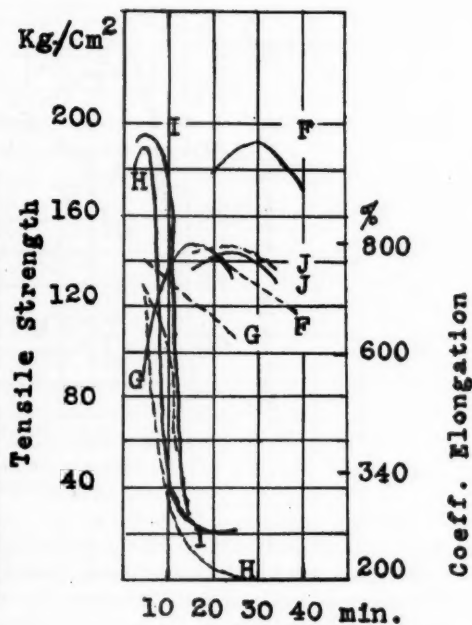


Figure 7—45 Lb./Sq. In.

— Tensile strength - - - % elongation

TABLE V

Sample	Smoked Sheet	Zinc Oxide	Sulfur	Diphenylguanidine	Mercapto-benzothiazole
F	100	10	5	1.000	0.000
G	100	10	5	0.915	0.085
H	100	10	5	0.558	0.442
I	100	10	5	0.425	0.575
J	100	10	5	0.000	1.000

TABLE VI

VULCANIZATION BY STEAM 45 LB./SQ. INCH PRESSURE (144°)

Sample	Time of Vulcanization, Min.	Tensile Strength, Kg./Sq. Cm.	Coeff. of Elongation, %
F	20	178.5	776
F	30	193.8	719
F	40	172.0	669
G	5	88.0	760
G	15	147.3	693
G	25	132.9	625
H	5	190.2	719
H	15	23.3	245
H	25	20.7	202
I	5	197.5	707
I	10	185.5	617
I	15	25.3	251
J	15	134.6	780
J	25	150.0	789
J	35	130.5	742

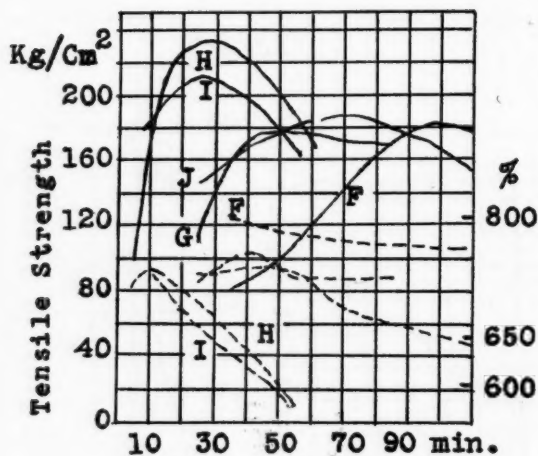


Figure 8—20 Lb./Sq. In.

— Tensile strength - - - % elongation

gasoline from each sample into a graduated cylinder, which was placed above a cobalt glass over a 10-candle power electric bulb with a carbon filament (using 0.3 amperes a. c.) until the filament was no longer visible. The height of the gasoline column (Tables III and IV) indicates the reciprocal turbidity. Figures 2-6 indicate that there was no scorching by vulcanization at 70° C., since only

TABLE VII
VULCANIZATION BY STEAM 20 LB./SQ. INCH PRESSURE (125°)

Sample	Time of Vulcanization, Min.	Tensile Strength, Kg./Sq. Cm.	Coeff. of Elongation, %
F	35	82.0	802
F	50	103.4	791
F	65	146.2	781
F	80	170.1	775
F	95	186.2	773
F	100	180.8	767
G	25	115.0	725
G	40	175.3	764
G	55	181.8	782
G	70	174.6	735
G	85	175.3	735
H	5	98.2	719
H	10	165.0	741
H	15	215.7	726
H	30	234.6	691
H	45	215.4	626
H	60	170.8	565
I	10	135.5	738
I	25	213.2	668
I	40	198.7	626
I	55	165.5	572
J	25	148.5	731
J	40	174.1	741
J	55	198.8	737
J	70	190.8	692
J	85	183.2	682
J	110	159.6	655

sample C showed, at the right end, a slight tendency. However, at 100° C. all showed scorching. Samples A and E started scorching after approximately 70 minutes, and B after 50 min., whereas C and D showed rapid scorching after 15 minutes. In short the molecular compound showed the strongest scorching, the mixture D, which is closest to the molecular compound, showed the second strongest scorching, and the scorching for the single accelerators was least.

(c) *Vulcanization by Steam Pressure at 20 and 45 Lb. per Square Inch.*—Diphenylguanidine and mercaptobenzothiazole were mixed as in Experiment b, milled according to the standard method specified by the Committee of Rubber Chemistry of the American Chemical Society, and vulcanized at 20 and 45 lbs. pressure per square inch. The compounds are shown in Table V. The results of the press-vulcanization at 45 lbs. steam pressure per square inch are shown in Table VI, and those of 20 lbs. per square inch in Table VII. These results indicate that sample H showed the best acceleration, samples I and G followed, and the single accelerators gave the least acceleration. Although Thiollet and Martin showed that the combined use of diphenylguanidine and mercaptobenzothiazole increased the smoothness of vulcanization, our experiment showed that such tendencies were more or less lost.

Summary

1. The effect of acceleration by the combined use of accelerators was studied with the aid of eutectic curves.
2. Diphenylguanidine and mercaptobenzothiazole form a molecular compound at their molecular ratio of 1:1, and this compound showed the strongest acceleration. Higher activity of combined accelerators is not attributed to their lower melting point, since the molecular compound melts at a higher point than the eutectic mixtures.
3. The accelerators which gave the maximum acceleration also gave maximum scorching.

II. Mercaptobenzothiazole and Methylene-Aniline

Kitaro Kojima and Izumi Nagai

In the preceding article, we described the results obtained with mercaptobenzothiazole and diphenylguanidine by the use of eutectic mixtures of the two different eutectic points and the one molecular compound in their eutectic curve, and the effect which these substances had on the scorching and acceleration of the rubber. The molecular compound showed a marked accelerating action and also strong scorching, but we were unable to obtain a definite result from the use of eutectic mixtures. This experiment includes the same work on methylene-aniline and mercaptobenzothiazole. Further work on another accelerator is in progress.

Experimental Procedure

(a) *Finding the Eutectic Curve.*—Mercaptobenzothiazole and methylene-aniline mixed in different ratios were placed in a capillary tube (1 mm. diam.) to a height of 5 millimeters. The substance was heated in a sulfuric acid bath, and the temperature of the softening point and the complete melting point were noted. Commercial mercaptobenzothiazole after recrystallization three times from benzene,

melted at 178° C. Methylene-aniline, $\text{C}_6\text{H}_5\text{N} \cdot \text{CH}_2 \cdot \text{N}(\text{C}_6\text{H}_5) \cdot \text{CH}_2 \cdot \text{NC}_6\text{H}_5$, was prepared by dissolving 50 cc. of aniline in 500 cc. of alcohol. While cooling and stirring, 50 cc. of 40 per cent formaldehyde were added and the mixture was allowed

to stand overnight. White needles recrystallized from benzene with melting point of 140.5°. The softening and melting points of mercaptobenzothiazole and of methylene-aniline are shown in Table I and Fig. 1. The mixture containing above

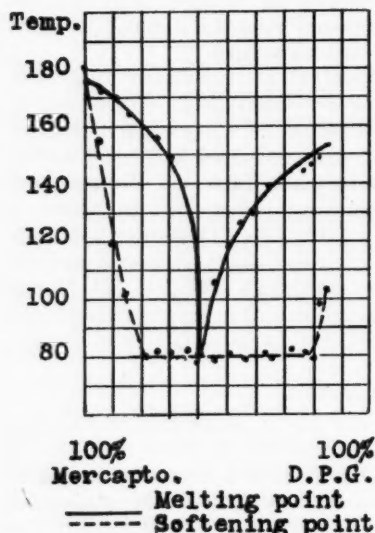


Figure 1

85 per cent of methylene-aniline and below 15 per cent of mercaptobenzothiazole became considerably colored, probably from decomposition by heating. Therefore no accurate estimation was possible, and no further experiment was attempted above this ratio. From the data in Table I and Fig. 1, it is shown that these two substances do not form a molecular compound and that there is only one eutectic point, which is at 59.0 per cent of mercaptobenzothiazole and 41.0 per cent of methylene-aniline. The scorching effect of these eutectic mixtures on ten rubber samples were as follows:

(b) *Studies of Scorching.*—The scorching test was carried on as outlined by Thies, and as described in the preceding experiment. The compounding is shown in Table II. In compounding sample No. 7, shown in Table II, the two accelerators were used in the ratio of their eutectic mixtures, as found in Table I and Fig. 1. All

the samples of the above compounds were milled and pressed to 0.1 cm. thickness, were left for a time, and were then cut into round disks of 1.6 cm. diameter. These samples were vulcanized at 70° and 100° C. in an oil bath for different times.

TABLE I

PER CENT BY WEIGHT			
Mercapto-benzothiazole	Methylene-aniline	Softening Point	Melting Point
100.0	0.0	...	178°
95.0	5.0	155°	172
90.0	10.0	120	170
85.0	15.0	102	165
78.1	21.9	79	160
75.0	25.0	81	155
70.0	30.0	81	149
60.0	40.0	78	100
55.0	45.0	78	105
49.0	51.0	80	118
45.0	55.0	79	126
40.0	60.0	78	130
35.0	65.0	79	139
30.0	70.0	80	142
27.5	72.5	82	144
22.5	77.0	81	144
20.0	80.0	97	146
17.5	82.5	99	149
15.0	85.0	103	153
0.0	100.0	...	140.5

The samples thus heated were placed in large test tubes containing 50 cc. of gasoline (d. 0.767 at 14.5° C.) and stirred 100 times per minute. The solutions were then

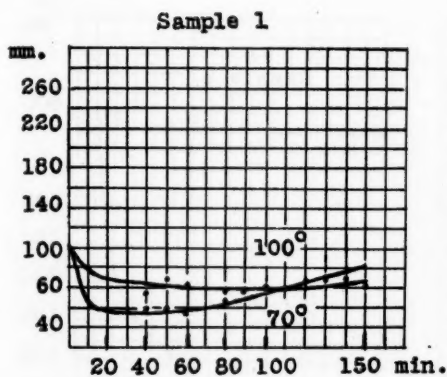


Figure 2

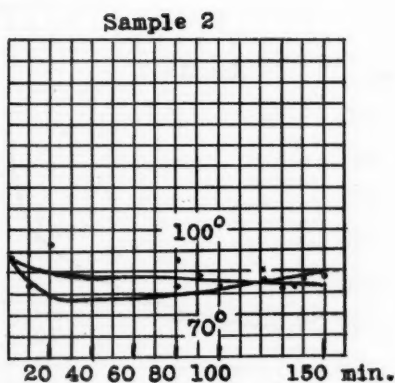


Figure 3

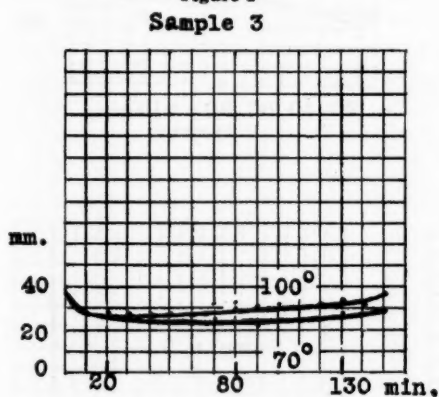


Figure 4

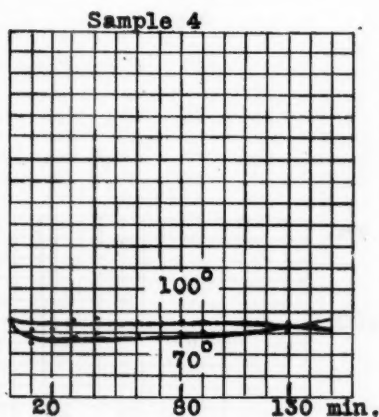


Figure 5

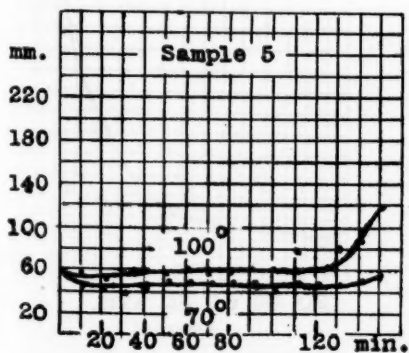


Figure 6

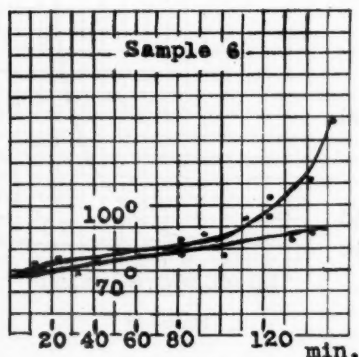


Figure 7

poured in a turbidimeter tube, which was placed above a cobalt glass, under which a 10-candle power carbon filament electric bulb (using 0.3 ampere a. c.) was placed, until the filament was no longer visible. The results are shown in Figs. 2-11.

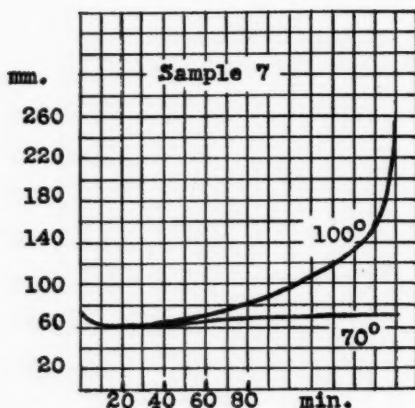


Figure 8

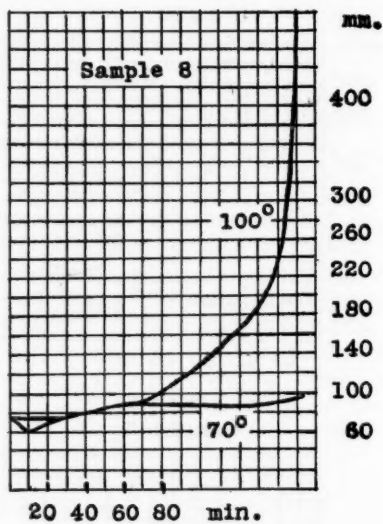


Figure 9

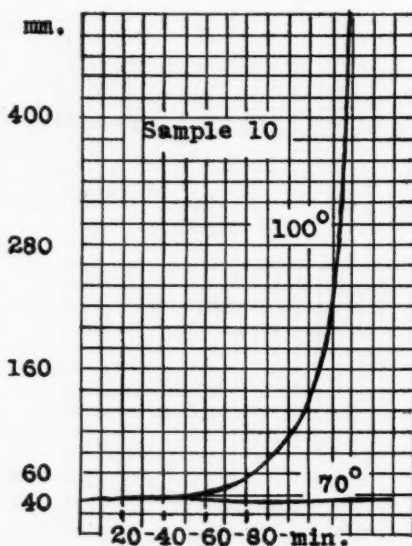


Figure 10

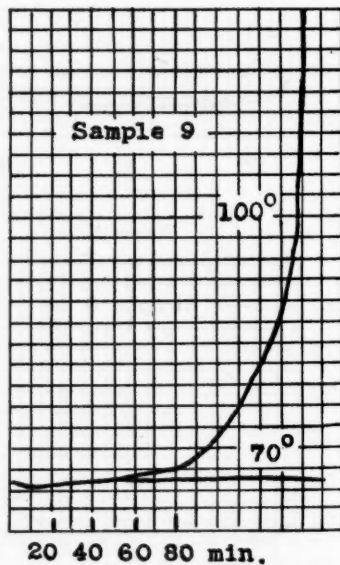


Figure 11

These results indicate that the eutectic mixture does not show any special characteristics either at 70° or 100°. At 70° it showed no scorching, but at 100° showed increasing scorching with increasing additions of mercaptobenzothiazole.

TABLE II
COMPOUNDING (BY WT.)

Sample No.	Smoked Sheet, %	Zinc Oxide, %	Sulfur, %	Accelerator		
				Total, %	Mercapto-benzothiazole, %	Methylene-aniline, %
1	100	100	5	1	0.00	100.00
2	100	100	5	1	8.12	91.88
3	100	100	5	1	15.05	84.98
4	100	100	5	1	20.65	79.04
5	100	100	5	1	34.65	65.00
6	100	100	5	1	45.00	55.00
7	100	100	5	1	59.00	41.00
8	100	100	5	1	70.00	30.00
9	100	100	5	1	85.00	15.00
10	100	100	5	1	100.00	0.00

TABLE III
VULCANIZATION BY HEAT AT 70°

Time of Heating, Min.	Reciprocal Conductivity of the Samples, Mm.									
	1	2	3	4	5	6	7	8	9	10
0	110	93	75	72	59	55	76	73	47	34
10	72	95	55	63	46	67	60	60	41	39
20	72	105	55	64	44	100	65	73	49	35
30	70	75	50	72	39	57	66	81	49	39
40	56	80	46	72	44	65	69	75	49	35
50	69	75	55	70	49	74	61	85	49	32
60	65	75	46	70	48	73	66	89	47	33
70	58	74	50	70	48	73	65	91	48	29
80	58	90	59	70	48	86	71	90	47	31
90	58	74	42	70	48	93	69	89	47	31
100	61	64	62	70	43	71	59	91	50	28
110	61	70	48	71	47	86	69	89	61	34
120	65	71	55	70	47	84	61	87	56	35
130	68	64	55	68	46	86	74	100	46	35
140	61	74	65	70	50	95	65	86	46	31
150	61	65	59	65	54	72	69	96	45	30

TABLE IV
VULCANIZATION BY HEAT AT 100°

Time of Heating, Min.	Reciprocal Conductivity of the Samples, Mm.									
	1	2	3	4	5	6	7	8	9	10
0	106	93	70	72	59	55	76	73	47	34
10	43	69	54	51	56	62	62	82	40	34
20	35	56	55	57	51	70	61	85	45	36
30	35	65	55	57	56	70	67	89	47	37
40	39	65	56	60	59	68	67	80	50	33
50	40	53	52	56	59	75	71	84	48	..
60	36	54	62	57	60	79	90	93	52	40
70	41	55	66	58	56	80	75	88	54	48
80	46	65	66	59	59	73	90	100	59	..
90	58	60	61	62	62	80	90	106	64	56
100	62	68	59	60	62	86	98	134	130	104
110	62	75	..	72	79	108	105	..	125	125
120	66	80	62	65	60	128	129	175	168	120
130	66	75	68	65	82	106	136	190	250	..
140	69	75	65	70	90	144	151	240	370	..
150	80	75	74	78	120	198	325

Vulcanization at 20 lbs./sq. inch

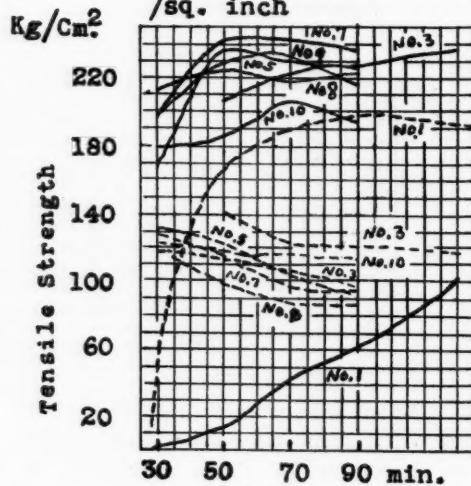


Figure 12

— Tensile strength - - - - Coeff. of elongation

TABLE V
COMPOUNDINGS OF RUBBERS FOR VULCANIZATION IN STEAM

Sample No.	Smoked Sheet, %	Zinc Oxide, %	Sulfur, %	Accelerator		
				Total, %	Mercapto-benzothiazole, %	Methylene-aniline, %
1	100	100	5	1	0.0	100.0
3	100	100	5	1	15.0	85.0
5	100	100	5	1	34.6	65.4
7	100	100	5	1	59.0	41.0
8	100	100	5	1	70.0	30.0
9	100	100	5	1	85.0	15.0
10	100	100	5	1	100.0	0.0

TABLE VI
MECHANICAL STRENGTH OF RUBBERS VULCANIZED BY STEAM AT 20 LB./SQ. IN.

Sample No.	Time of Vulcanization, Min.	Tensile Strength, Kg./Cm.²	Elongation, %	Sample No.	Time of Vulcanization, Min.	Tensile Strength, Kg./Cm.²	Elongation, %
1	30	3.4	580	3	50	206.0	830
1	50	12.2	881	3	70	222.0	792
1	70	42.2	926	3	90	227.0	789
1	90	60.2	947	3	120	235.0	779
1	120	101.8	932	7	30	196.0	797
5	30	165.5	813	7	50	242.0	780
5	50	236.0	794	7	70	243.0	743
5	70	229.0	757	7	90	236.0	738
5	90	227.0	735	9	30	196.0	787
8	30	212.0	791	9	50	229.0	777
8	50	224.0	747	9	70	232.8	760
8	70	217.8	725	9	90	215.5	743
8	90	222.2	722				
10	30	179.6	806				
10	50	183.5	780				
10	70	205.0	785				
10	90	193.5	782				

Vulcanization at 45 lbs. /sq. inch

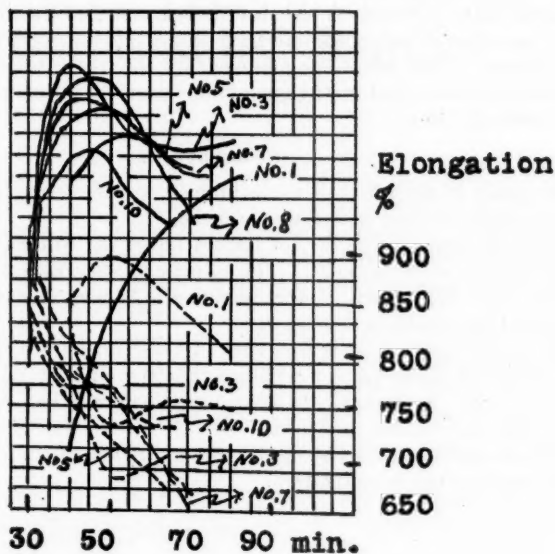


Figure 13

— Tensile strength - - - - - Coeff. of elongation

TABLE VII

MECHANICAL STRENGTH OF RUBBERS VULCANIZED BY STEAM AT 45 LB./SQ. IN.

Sample No.	Time of Vulcanization, Min.	Tensile Strength, Kg./Cm. ²	Elongation, %	Sample No.	Time of Vulcanization, Min.	Tensile Strength, Kg./Cm. ²	Elongation, %
1	15	28.9	843	3	15	154.5	847
1	25	93.7	897	3	25	179.8	733
1	40	136.0	855	3	40	173.0	755
1	45	159.5	804	3	55	178.0	747
5	5	69.0	849	7	5	99.2	904
5	15	200.0	758	7	15	214.0	815
5	25	194.5	722	7	25	191.5	777
5	45	166.0	673	7	45	165.0	653
8	5	122.5	855	9	5	123.0	884
8	15	203.0	769	9	15	186.0	786
8	25	206.0	770	9	25	192.5	682
8	45	138.5	697	9	40	169.0	702
10	10	153.5	801				
10	20	174.5	771				
10	30	152.5	744				
10	40	187.5	730				

(c) *Vulcanization Experiment at 20 and 45 Lb. Steam Pressure per Square Inch.*— The result of the vulcanization test is shown in Figs. 12-13 and Tables VI-VII, and shows that the eutectic mixture gives the strongest acceleration and a smooth vulcanization. The merit of the combined use of two accelerators at the different ratios may be attributed to the lowering of their melting points which causes them to diffuse better and increase the vulcanization effect, and this effect becomes greatest when the two are mixed at a ratio which forms their eutectic mixture. It is con-

sidered that the use of two eutectic mixtures of mercaptobenzothiazole and diphenylguanidine gave no noticeable vulcanization acceleration in the previous experiment. This may be due to the relatively slight lowering of the melting point at their eutectic point. Moreover the accelerating action of the molecular compound may have been too strong, and may have destroyed the accelerating effect of the eutectic mixture. This effect is made clear by the use of the eutectic mixture of mercaptobenzothiazole and methylene-aniline since the eutectic mixture showed a far lower melting point.

Summary

1. The study of the effect of the combined use of mercaptobenzothiazole and methylene-aniline is based on its eutectic curve.
2. These two accelerators do not form a molecular compound on mixing, and they have only one eutectic point. The eutectic mixture gave a stronger accelerating action than did either of the ingredients alone, vulcanization proceeded smoothly, and the products were superior.
3. The scorching effect increased with increase in the proportion of mercaptobenzothiazole, but there was no evidence that the eutectic mixture gave any increased scorching. In general, the scorching effect was less when these two accelerators were used in combined form.

The authors wish to thank Drs. Y. Ogawa and S. Minatoya for their kind advice during the course of this investigation.

Effect of Overmilling on Compounded Rubber

W. B. Wiegand

Introduction

The conviction seems more and more prevalent that the full reinforcing capabilities of fine pigments such as carbon black have not as yet been fully developed. A great deal of thought is therefore being devoted to the study of improved means of dispersion of such ingredients in rubber. The various conditions of grinding and the effect of dispersing agents are examples of the lines along which the modern study of this problem is progressing.

This naturally leads to the question of what is happening to the rubber phase during the dispersion process. In other words, what damage, if any, will overmastication do to the rubber quality? What influence do these conditions exert on aging behavior? What is the effect of mill opening during such mastication?

Early Experiments (1917)

The mixing contained fine para rubber, 100 parts; zinc oxide, 100 parts; litharge, 20 parts; and sulfur, 8 parts. The cure was 30 minutes at 40 pounds' steam pressure in a laboratory mold.

In one case the ingredients were milled in the regular way (20 to 25 minutes on the laboratory mill). In the other, the rubber and zinc oxide were allowed to run on the mill for exactly one hour after the zinc oxide had been taken up. The litharge and sulfur were then added (time five minutes), and the batch cut off. Cures were made 24 hours after mixing. The results were as follows:

TABLE I

	Unaged			Heat-Aged			Shelf-Aged 2 Years 3 Months		
	*	Δ	°	*	Δ	°	*	Δ	°
Regular milling	3000	595	179	2600	563	148	2330	530	123
Overmilled	2950	600	177	2525	550	134	2065	495	102

* = Tensile strength. Δ = Elongation. ° = Tensile product.

Shelf-aging means that the samples were placed on a shelf in a filing room exposed only to diffused interior light. All that can be concluded from this result is that on aging, particularly the natural aging, the physical properties of the overmilled specimen showed marked deterioration when compared with the control, whereas in the original condition there was no sensible drop either in tensile strength or in elongation with overmilling.

Second Series (1926)—Four Years' Natural Aging

In this case a carbon black mixing of the tread type was employed and contained: rubber, 93 parts; carbon black (Miconex), 35 parts; zinc oxide, 3 parts; sulfur 5 parts; and diphenylguanidine, 0.75 part.

In addition to the normal milling of 14 minutes for the above formula, samples were given an extra 60 minutes of grinding (approximately 400 per cent overmilling).

TABLE II
PHYSICAL PROPERTIES

General Procedure	Details of Milling			Condition of Raw Stock	Before Aging					After Aging			Remarks
	Time, Min.	Roll Temp.	Roll Gap		Modulus 400%	Tensile Strength	% Elongation	Tensile Product	Cure @ 40 Lb. Min.	Tensile	% Elongation	Acetone Extract, %	
Control normal milling	14	125° F.	Normal	Normal	1680	4200	690	290	30	950	320	7	Sample had fairly good stretch and odor. Acetone extract of normal odor
Overmilled milled Hot	60	300° F.	Same	Very soft and tacky	1580	4100	660	270	40				
Overmilled Cold	60	50° F.	Same	Very soft and tacky	1830	4200	630	265	60				
Over-refined Cold	60	50° F.	Tight as possible	Very soft and tacky	2280	4400	600	264	80				
					935	1400	490	69	30				
					1340	2400	570	137	40				
					1655	2600	530	138	60				
					1900	3000	510	153	80	725	50	25	Hard. Badly perished Bad odor. Extract malodorous
					910	1400	500	70	30				
					1330	2000	490	98	40				
					1700	2100	470	99	60				
					1950	2300	450	104	80	625	50	22	Much the same
					1070	1700	530	90	30				
					1400	2100	490	103	40				
					1900	2300	450	104	60	750	75	26	Almost the same Somewhat better elongation
					1910	2300	440	101	80				

The temperature was varied in one case by circulating steam at 300° F. ("hot overmilling") and in the other case, water at about 50° F. ("cold overmilling"). The temperature of the rubber was not determined in this experiment, but more recent tests have shown that the actual temperature differences in the rubber itself were of the same order as those of the mill rolls.

The gap between the mill rolls was normal ($\frac{3}{16}$ in.) except for one batch in which the rolls were closed up as tightly as possible so as to approximate "refining" conditions. In the latter case the "bank" was kept active by frequent cutting.

The accelerator was added to the mix as soon as the rubber ran smooth. Then the carbon black and zinc oxide were incorporated. The sulfur was in all cases added at the end. The technic of testing was virtually that adopted by the Physical Testing Committee, American Chemical Society (*Rubber Age*, January 25, 1930).

The tests are summarized in Table II.

The 30 minutes' cure chosen for the control mixing was based on many years' experience with the formula in question, but the selection of the proper cure for the overmilled samples was, at best, a compromise. Prolonged milling doubled the time of cure to the approximate physical optimum. The cures actually chosen were on the near side of the physical optimum, *i. e.*, they corresponded to a condition where both tensile strength and tensile product were still rising.

The 80 minutes' cure for hot and cold overmilling and the 60 minutes' cure for cold over-"refining" were selected as being the shortest which had developed even moderate unaged tensile strengths. In addition to the retardation in curing rate, the physical properties in general showed a severe drop in quality.

Samples were stored away from direct light, at room temperature, for four years. At the end of this time all the overmilled samples had turned hard, resinous, and malodorous. The physical properties had fallen to very low figures. The normally milled sample, although low in tensile strength, still showed excellent stretch and was distinctly rubbery and not malodorous.

The acetone extracts, both as to amount and character, also confirmed the damage done by the excessive mastication.

A study of these results indicated, in addition to severe deterioration on natural aging, an unexpectedly marked fall-off in the unaged physical properties. This difference seemed so marked, compared to the preliminary experiments done in 1917, that it seemed worth while to repeat the whole series, first with diphenylguanidine present during the overmilling, and second with the accelerator left out.

Third Series (1931)

Although by no means typical of modern tire tread compounding practice, the mixing employed in the 1926 series was again used. Temperatures of the mill rolls in the case of both hot and cold overmilling were adjusted to duplicate as closely as possible the second series. In the case of the control the temperature of mixing was 125° F., the time of incorporation 12 minutes. The accelerator was added at the beginning and sulfur at the end. Hot overmilling was done at 300° F. for one hour; cold overmilling at approximately 50° F., also for one hour.

Overmilling without Accelerator

In this case all the ingredients were milled in excepting the accelerator and sulfur, these being added on the day after the overmilling took place. In all cases the batch was cut continuously so as to maintain an active bank. All batches were rested 48 hours before curing. The results are shown in Table III.

TABLE III
EFFECT OF OVERMILLING (BEFORE ADDING DIPHENYLGUANIDINE)

Cure, Min.	Control Normal Milling (12 Min.)			Hot Overmilling (60 Min.)			Cold Overmilling (60 Min.)			Cold Overmilling (60 Min.)— Nip Closed		
	Modu- lus 300%	Tensile Strength	Elon- ga- tion Product	Modu- lus 300%	Tensile Strength	Elon- ga- tion Product	Modu- lus 300%	Tensile Strength	Elon- ga- tion Product	Modu- lus 300%	Tensile Strength	Elon- ga- tion Product
30	900	4600	710	1300	3700	530	700	3100	630
40	1050	4700	680	1450	3900	525	1050	4200	650	975	2700	535
60	1300	4600	615	1650	4300	550	1300	4500	630	1100	2800	510
80	1450	4600	610	1550	3800	510	1400	4200	580	1200	2500	470

TABLE IV
EFFECT OF OVERMILLING (WITH DIPHENYLGUANIDINE)

Cure, Min.	Control Normal Milling (12 Min.)				Hot Overmilling (60 Min.)				Cold Overmilling (60 Min.)				Cold Overmilling (60 Min.)— Nip Closed			
	Modu- lus 300%	Tensile Strength	Elon- ga- tion	Tensile Product	Modu- lus 300%	Tensile Strength	Elon- ga- tion	Tensile Product	Modu- lus 300%	Tensile Strength	Elon- ga- tion	Tensile Product	Modu- lus 300%	Tensile Strength	Elon- ga- tion	Tensile Product
30	900	4600	710	324	475	1800	530	96	700	3200	650	208
40	1050	4700	680	319	575	2000	530	106	875	3600	630	226	775	2200	505	110
60	1300	4600	615	283	725	2400	530	127	1100	4200	650	273	1050	2500	500	125
80	1450	4600	610	280	800	2600	540	140	1250	4100	610	250	1150	2300	480	125

The effect of one hour's hot overmilling is seen to be a decrease in the tensile strength and in the elongation at rupture, together with a retardation in the time of physical optimum from 40 minutes to 60 minutes. The modulus at 300 per cent was, however, markedly increased.

Cold overmilling gave results similar in kind but less marked.

Cold overmilling with the rolls tight (refining) was much more severe than either hot or cold overmilling with normal gap. Although the modulus was substantially unchanged, the tensile strength dropped nearly one-half, and the elongation was also seriously affected.

Overmilling in the Presence of Diphenylguanidine

In this case the overmilling was carried out in the presence of diphenylguanidine. The results are shown in Table IV.

Hot overmilling in the presence of the accelerator retarded the physical optimum to 80 minutes or more. The modulus, tensile strength, and elongation at rupture were all seriously lowered. Clearly in the presence of the accelerator the effect of hot overmilling was disastrous to the rubber quality, even in the unaged condition.

On the other hand, cold overmilling, though lowering the physical properties compared either to the control or to the cold overmilling without the accelerator, worked much less damage than in the preceding case.

Cold overmilling with tightly set rolls behaved in general as in the preceding case. The presence of the diphenylguanidine lowered the properties compared to cold overmilling itself, but not to any striking extent.

From this series it is evident that overmilling with diphenylguanidine present is capable of doing more damage than overmilling before adding the accelerator as far as unaged properties are concerned.

Herein lies at least part of the explanation of the difference between the early experiments and the second series. The original compound contained no diphenylguanidine or other organic accelerator, and consequently showed little fall-off in unaged physical properties. On the other hand, the second series contained diphenylguanidine.

The resistance to tear, determined approximately by hand testing, seemed to have suffered more deterioration in the case of almost all of the overmilled specimens than would have been expected from the tensile strength figures.

Samples of this series are being laid away for future examination as to natural aging.

General Conclusions

(1) Whenever, in order to obtain pigment dispersion there is need for prolonged mastication or mixing, this should be carried out at a relatively low temperature and without organic accelerator.

(2) Such mixing should be reduced to the shortest possible time as it causes injury both to immediate properties and to aging properties. This injury is of a subtle character, in that it may not show up in the tensile strength values.

(3) The practice of preparing carbon black tread mixings by means of, first, a short masterbatch operation followed by a cooling off or resting period; and then, secondly, by a mixing stage, during which the remaining ingredients are added, would seem in the light of the foregoing experiments to achieve the desired dispersion with least injury to the rubber substance.

The Elasticity Constants of Rubber under High Tensions

Rudolf Weise

LEIPZIG

Introduction

The problem of determining the elasticity constants of rubber involves various difficulties. Since the material under investigation frequently has very different chemical properties, even when under the same name, no wholly consistent results are to be expected of physical tests. Moreover, it has been found by experience that tests of samples cut from the same sheet differ greatly. Ordinarily these variations must be accepted as inevitable. However, as the present work will show by way of example, these variations can be kept within certain limits through a proper utilization of a number of experiments.

From a technical point of view, the study of elasticity is concerned chiefly with the properties of isotropic substances. Since, upon stretching, rubber becomes anisotropic, the question naturally arises whether mathematical formulas which are valid for isotropic substances have in general any meaning when applied to rubber. Furthermore, it should be mentioned at the beginning that Scherrer¹ has proved by x-ray photographs that in the unstretched state rubber is an amorphous substance. Only at an elongation of about 100 per cent do interferences appear, so that, at least for our purpose, rubber can be regarded as "quasi-isotropic" up to this degree of elongation. This may also be justifiable to a certain extent even at higher elongations since, in describing the elastic properties, the volume is the only function used besides direct measurements, and the volume changes at the most only 2 per cent up to the highest elongations.

A large amount of work has been done on the modulus of elasticity and the Poisson constant of rubber. An examination of the literature at present showed, however, that measurements cover at the most only a small part of the possible range of elongation. Only Bjerken² and Villari³ have undertaken experiments at higher elongations as well. The latter investigated the modulus of elasticity up to 6 times, the former the Poisson constant up to 5 times the initial length.

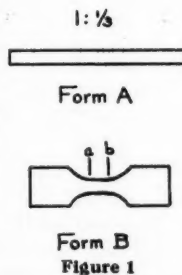
The object of the present work therefore has been to determine both constants of elasticity, *viz.*, the modulus of elasticity and the Poisson constant, over the entire range of elongation, with particular attention to determinations of the modulus of elasticity just previous to rupture. To eliminate the temporary after-effect a kinematographic method of measurement was used to advantage. By the same method it was possible to obtain data upon the behavior of rubber up to the point of rupture. To complete the picture of elastic properties, the permanent set as a function of the time and tension was determined.

Procedure

In these experiments on elongation, rubber known commercially as "Pure para sheet" was used exclusively. (Hot vulcanized samples of "pure gum quality" were used. Specific gravity determinations of 3 different samples showed 0.923, 0.945, and 0.938 gram per cubic centimeter.) The samples were of two shapes, as shown in Fig. 1. When the prismatic strips were used (Form A), rupture always took

place close to the point of clamping. Accordingly, in experiments at high elongations Form B was used. Since the results might depend upon the form of the samples, several series of experiments were carried out with both forms. There was satisfactory agreement in the results with the two shapes of test pieces.

A die was used to prepare samples of Form B. Because of the characteristic property of rubber of spreading out under the pressure of the die, resort was had to conical cutting. In order to minimize the errors from this cause, rubber only 1 millimeter thick was used. This led immediately to a second difficulty. On account of the great tendency to deformation of rubber, it was generally impossible to hold the sample in the clamps throughout the elongation. Through the choice of thin sheets of only one millimeter thickness it was unnecessary to support the clamps even up to the point of rupture. A slipping of a few millimeters could not be avoided. The brass clamps were provided on the inside with grooves and could be brought together very tightly by means of two wing screws. To avoid the effect of friction, the samples, clamps, and weighing scale were so arranged that they hung freely. In determining the length a cathetometer with a scale 1 meter high was used to measure the distance between two ink marks. The section to be measured was in the middle of the sample between the two clamps. In the case of samples of Form B, the marks were placed within the prismatic part, a-b. Since the width of the marks and their spreading during elongation gave rise to considerable inaccuracy, at least two readings were taken on the upper and lower edges of every mark.



The Elastic Limit

By perfect elasticity is meant that ability of a substance to resume its original form after deformation by an external force when the external force is removed. Since, however, most substances show a permanent set after even small elongations, the idea of *elastic limit* has been introduced. This corresponds to the elongation which brings about a permanent elongation of a definite magnitude. Thus in the case of Krupp steel, that strain which brings about a permanent elongation of 0.03 per cent has been designated as the elastic limit.

In order to study the permanent elongation of rubber that has been stressed and then released, ten test pieces of Form "A" were cut in the same direction from a sheet of rubber one millimeter thick. After measuring the length before applying any stress, the ten samples were subjected to stresses of 100, 200, up to 1000 grams for two hours, after which their lengths were measured. After release, measurements were made of the permanent elongation after 2 hours, after 24 hours, and after about one year. These loads correspond to elongations of approximately 0.01 to 0.1 kilogram per square millimeter, based on the original cross section, or 0.01 to 0.4 kilogram per square millimeter based on the cross section at the time. Table I gives the values obtained, and shows that up to about 100 per cent elongation the rubber may be regarded as "perfectly" elastic. Recovery from its initial "permanent" elongation required, however, a relatively long time. Because of this large temporary after-effect, it might be advisable to establish a standard time for comparative measurements, at the end of which time the permanent elongation might be measured.

It should be mentioned here that the degree of elongation (approximately 100 per cent), beyond which there is an appreciable permanent set, coincides approxi-

mately with that elongation at which the appearance of x-ray interferences has been observed.

TABLE I
Length in % of the Unstretched State

Sample (Form A) Number	Load in G.	After 2 Hrs. Load	2 Hrs. after Release	24 Hrs. after Release	About 1 Year after Release
1	100	110.6	100.14	100.05
2	200	125.6	100.31	100.12	100.01
3	300	149.6	100.43	100.15	100.04
4	400	184.0	100.49	100.02?	99.98
5	500	216.5	100.71	100.28	99.99
6	600	261.6	101.04	100.47	100.41
7	700	301.3	101.62	100.89	100.52
8	800	397.6	101.68	100.92	100.22?
9	900	429.4?	101.41?	100.99	100.68
10	1000	410.6	101.76	101.19	100.73

The Poisson Constant

To determine the ratio of the cross-sectional contraction to the increase in length, a dividing machine with microscopic readings was used to measure the width. The distance between the marks mentioned above served to measure the length, and the total width of the strip in the same region served as a measure of the width. In order to minimize the errors in measuring the changes with time, the measurements were not made until 30 minutes after application of the load. Pulfrich⁴ has shown that the temporary after-effect has no influence on the value of the Poisson constant. From the final values observed the "differentially" defined value μ can be calculated in the following manner.⁵

$$\frac{db}{dl} = -\mu \frac{b}{l}$$

where b is the breadth and l is the length.

Integration between the initial state a and any final state c :

$$\int_a^c \frac{db}{b} = -\mu \int_a^c \frac{dl}{l}$$

gives

$$\mu = \frac{\log \left(\frac{b_c}{b_a} \right)}{\log \left(\frac{l_c}{l_a} \right)}$$

The values given in Table II were obtained with three samples of Form A, while the values in Table III were obtained with three samples of Form B. In both tables the μ values give the mean value $\mu_M = 0.490$. With an isotropic substance, the Poisson constant μ is 0.5 the constant volume. In connection with the measurements of the modulus of elasticity given in the following part, in order to be certain that the calculations may be made with approximately constant volume (*i. e.*, also with the value 0.5 for the contraction at right angles to the direction of our measurement) the following test measurement was made. The specific gravity of two unstretched samples of Form A was determined. After the samples had been stretched six to seven times their length on a brass support of known weight, two measurements were made. Both these experiments gave a decrease in volume of 1.4 and 1.7 per cent, respectively. Although the accuracy of this measurement is none too great, it still shows that the change in volume was very slight compared with the great capacity of deformation of the rubber. For this reason in the following work rubber is considered to remain unchanged in volume.

TABLE II

Sample (Form A) Number	Load in G.	Width in Cm.	Length in Cm.	Length in % of the Un- stretched State	μ
1	0	1.010	0.572	100	...
	100	0.963	0.630	110	0.493
	200	0.901	0.716	125	0.509
	300	0.833	0.846	148	0.492
	400	0.762	1.028	180	0.481
	500	0.686	1.270	222	0.485
	750	0.566	1.896	331	0.483
	1000	0.500	2.437	426	0.485
2	0	1.093	1.041	100	...
	500	0.769	2.183	210	0.475
	1000	0.546	4.246	408	0.494
	1500	0.465	5.686	546	0.503
	2000	0.453	6.462	621	0.482
	2500	0.436	6.950	668	0.484
3	0	0.984	1.094	100	...
	2500	0.380	7.776	711	0.485
	3000	0.376	8.081	739	0.481
	4000	0.363	8.531	780	0.486

TABLE III

Sample (Form B) Number	Load in G.	Width in Cm.	Length in Cm.	Length in % of the Un- stretched State	μ
1	0	0.968	0.266	100	...
	100	0.916	0.298	112	0.486
	200	0.856	0.338	127	0.513
	300	0.784	0.399	150	0.520
	400	0.709	0.500	188	0.493
	500	0.638	0.628	236	0.485
	600	0.582	0.760	284	0.487
	700	0.542	0.883	332	0.485
2	0	0.897	0.067	100	...
	500	0.591	0.160	239	0.479
	750	0.489	0.234	349	0.485
	1000	0.426	0.314	469	0.482
	1100	0.409	0.337	503	0.485
	1200	0.401	0.355	530	0.483
	1300	0.379	0.381	569	0.496
	1400	0.369	0.405	605	0.494
	1500	0.365	0.415	619	0.493
3	0	0.950	0.079	100	...
	3000	0.344	0.616	780	0.495
	5000	0.331	0.662	838	0.496
	6000	0.329	0.675	854	0.494
	7000	0.324	0.688	871	0.497

The Modulus of Elasticity

In the case of metals, with their relatively small deformations, there is no hesitancy in applying the Hooke law in finite form and in basing the modulus of elasticity on the total load, and on the length and cross section in the unloaded state. This is not true of rubber with its great deformation, to which attention has already been called by Röntgen.⁶ It is recommended in this case, where the load is applied in steps, always to calculate the specific elongation so that the length reached at a

definite stress serves as the initial length in the calculation of the next step. Correspondingly only the additional load represents the load applied. In this case the Hooke law is used in its differential form.

$$\frac{dP}{Q} = E \frac{dl}{l} \quad (1)$$

where dP is the additional load, dl the resulting elongation, l the length at which the additional load is applied, and Q is the cross-section at the time of the application of the additional load. Accordingly in expressing the results on a numerical basis, it is necessary to use the new cross-section resulting from the previous deformations. The knowledge of the constancy of volume makes it possible to replace in Equation 1 the variable cross section Q by V/l . This gives the equation:

$$dP = EV \frac{dl}{l^2} \quad (2)$$

Within a moderate range (load) it is allowable to assume that E is a constant. Then Equation 2 can be integrated, and one obtains:

$$E = \frac{P_2 - P_1}{V \left(\frac{1}{l_1} - \frac{1}{l_2} \right)} \quad (3)$$

Experimental Results

Table IV gives the elongations of five different samples of Form A under loads of 100 to 800 grams, and also the moduli of elasticity calculated by Formula 3. The values for the different samples agree fairly well for the same load. The deviations found in all cases may originate therefore in part in the fact that, in calculating the volume by Formula 3, the thickness was assumed to be one millimeter throughout. Actually the thickness varied a few per cent, which naturally resulted in deviations in the elongation. On the other hand, the average thickness was very close to 1 millimeter. With two larger samples (approximately 4×10 centimeters and 10×15 centimeters from the same sheet out of which the samples were obtained), values of 0.998 and 1.005 millimeters were obtained by means of specific gravity determinations (0.9355 and 0.9365 gram per cubic centimeter).

TABLE IV

Sample (Form A)	No. 1	No. 2	No. 3	No. 4	No. 5	Average Value
Original width	10.44	10.55	10.26	10.48	10.72	10.49
Load in G.	Length in % of the Unstretched State					
100	110.8	110.0	110.3	110.1	110.8	110.4
200	126.1	123.9	124.3	124.4	125.0	124.7
300	145.3	142.4	143.4	144.1	144.9	144.0
400	173.1	169.1	170.1	172.2	173.3	171.6
500	211.1	203.7	205.1	208.8	210.3	207.8
600	254.4	244.2	247.1	250.7	254.7	250.2
700	298.8	286.4	290.2	293.3	296.6	293.1
800	337.5	326.6	321.7	333.3	334.7	330.8
Load in G.	Modulus of Elasticity (Kg. per Sq. Mm.)					
100	0.098	0.107	0.104	0.104	0.096	0.102
200	0.088	0.092	0.095	0.092	0.091	0.092
300	0.091	0.091	0.091	0.087	0.085	0.089
400	0.087	0.085	0.089	0.084	0.083	0.086
500	0.092	0.094	0.097	0.094	0.092	0.094
600	0.119	0.116	0.117	0.119	0.113	0.117
700	0.165	0.157	0.160	0.165	0.168	0.163
800	0.251	0.221	0.244	0.233	0.243	0.238

Table IV shows that the value of the modulus of elasticity first diminishes somewhat with increasing load, until it reaches a minimum at about 70 per cent elongation, beyond which point it increases. It is shown in the following that the modulus of elasticity increases considerably with further increase in load.

In determining the modulus of elasticity, especially at high elongations, the temporary after-effect has a noticeably disturbing effect upon the results. This is especially true since the final length obtained with a definite load is used as the initial length in calculating the next load. Here there is the disturbing factor that the final length at a given load changes considerably with the time. In order to eliminate as much as possible the influence of this temporary after-effect, several measurements of the length, whose average value is designated l_1^A , were made as quickly as possible after the application of a load P_1 . After about 20 minutes, the lengths were determined again by several measurements at the same load P_1 . This mean value is designated l_1^B . With a new additional load ΔP , the total stress was increased to P_2 . In this way a length l_2^A was first determined, and after the time mentioned above a length l_2^B was determined. To calculate the modulus of elasticity E the following formula was then used:

$$E = \frac{P_2 - P_1}{V \left(\frac{l}{l_1^B} - \frac{l}{l_2^A} \right)} = \frac{(P_2 - P_1) l_1^B l_2^A}{V (l_2^A - l_1^B)}$$

The values obtained in this series of experiments are shown in Table V.

TABLE V
Sample (Form B). Original Width = 0.596 Mm.
Length in Per Cent of the Unstretched State

Load in G.	Shortly after Applica- tion of the Load	About 20 Min. after Application of the Load	Modulus of Elasticity (Kg. per Sq. Mm.)
2	684.6	687.3	0.24
4	767.5	773.9	13.7
6	821.2	828.2	28.0
8.5	876.8	880.9 ± 0.7	38.9
10	885.2 ± 0.2	Ruptured	283 ± 52

Since the time which elapsed between the application of the load and the taking of the first measurements was sufficient to cause a change in the elongation, measurement of the elongation was made kinematographically in order to eliminate this after-effect, which varied with the time. When the weights were placed on the scale pan, they brought about contact for an electric circuit which contained a small electromagnet. Through the working of the latter, the shutter of the optical lens (behind which was a powerful incandescent lamp) was opened according to requirements for $1/5$ to $1/25$ of a second. In this way application of the load caused a flash of light which was recorded on the film on one or two pictures as a blackening. In addition, a counter which was connected to the axis of a synchronous motor was also shown on the film. From the frequency of the alternating current machine which drove the motor, from the number of poles of the rotor and the conversion factor between the motor and counter, the time for the appearance of a number could be calculated.

The photographs reproduced in Fig. 2 are portions of such a film. The strips of rubber, the camera, the counters, and the electromagnets can be plainly seen. The measuring marks can also be seen faintly. On account of short exposure, the spot of light in photograph A (Fig. 2) which shows the application of a new load is

visible only on the middle pictures of the film. On the contrary, in the experiment which is represented by photograph B in Fig. 2 a somewhat longer time of exposure was chosen so that the spot of light was reproduced on two pictures of the film. On account of the extreme fineness of the photographic coating and the resulting sharper reproduction of the spots, positive film was used for the photographs.

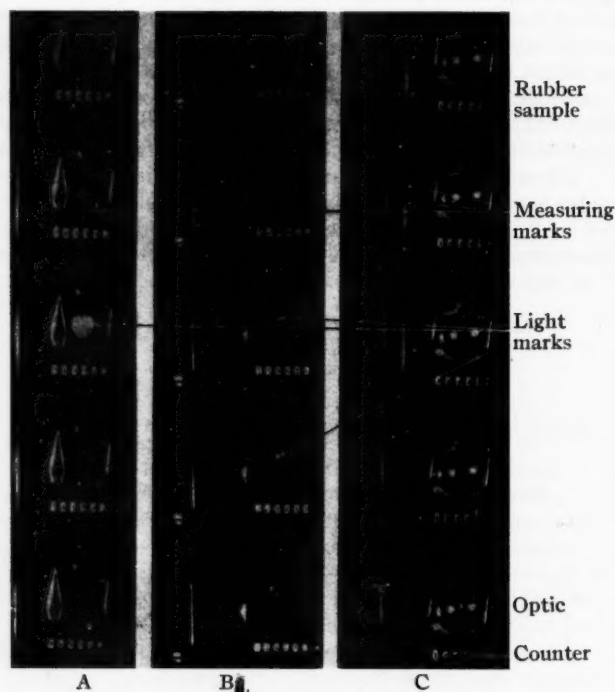


Figure 2

The distances were measured either by a comparator or with the fine adjustment of the cathetometer. The values for E obtained from such a film are shown in Table VI. Although the high value of the modulus of elasticity finally obtained cannot be considered very accurate, nevertheless it shows that rubber before rupture possesses a modulus of elasticity, along the direction of the stress, which is of about the same order of magnitude as that of wood.

TABLE VI
Sample (Form B). Original Width = 9.885 Mm.

Load in G.	Length in % of Unstretched State	Average of	Modulus of Elasticity (Kg. per Sq. Mm.)
7	800.00	25 film pictures	0.81
9	838.46	32 film pictures	35.3
10	854.61	23 film pictures	44.9
11.5	855.57	14 film pictures	ca. 1000

The Stress-Strain Diagram

By the aid of the relation: $V = Q_2 l_2$, equation 3 can be given in the form:

$$\frac{P_2 - P_1}{Q_2} = E \frac{l_2 - l_1}{l_1}$$

If the additional specific elongation: $\frac{l_2 - l_1}{l_1}$, is E' , and the additional stress $\frac{P_2 - P_1}{Q_2}$ is σ' , then a curve $\sigma' = f(E')$ can be drawn, from which the modulus of elasticity at every point can be obtained as the quotient $\frac{\sigma'}{E'}$. If the curve mentioned

represents a straight line through the origin of the coordinates, then this straight line shows that the modulus of elasticity is constant in the range concerned, and the slope gives its numerical value. Such a curve is shown in Fig. 3, the individual points on which are calculated from the values in Table IV. Although the modulus of elasticity is not quite constant (*loc. cit.*), an approximately straight line can be drawn through the origin and the points from 10 to about 100 per cent elongation. The slope of this line corresponds to a constant modulus of elasticity of 0.093 (kg./sq. mm.).

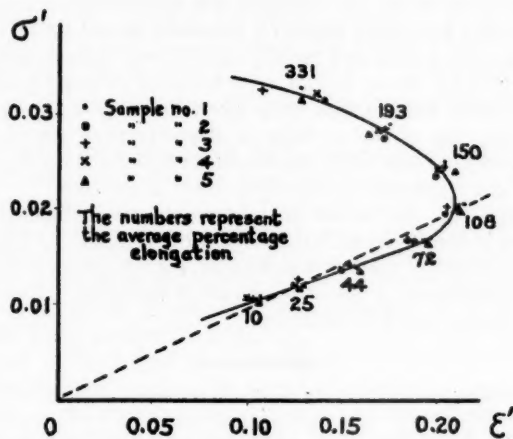


Figure 3

The modulus of elasticity begins to increase rapidly at about 100 per cent elongation. It is interesting that this rise begins at about the same degree of elongation at which x-ray interferences first become visible. At the same time the "arrangement" of the molecules increases the elastic resistance.

The Phenomenon of Rupture

In order to gain an insight into the nature and manner of rupture at its beginning, the attempt was made to photograph this phenomenon. Since rupture would have to take place within the small field of the photograph, a large number of experiments were necessary. In picture C (Fig. 2) the final stage in the experiment was recorded, where rupture occurred between the two measuring marks. According to the pictures, the rubber sample broke in the time between the photographing of the middle of one film and the following film. This time interval was calculated from the reading of the counter as 0.07 second. In all cases, rupture took place in a plane perpendicular to the elongation. There was no permanent diminution in cross-section, nor any permanent elongation at break worth mentioning. It may

therefore be definitely said that a previous constriction of the section at break does not take place. Furthermore, since the originally smooth surface of the samples showed no visible change after rupture, all properties⁷ are present which are characteristic of a brittle substance. Accordingly rubber is brittle before rupture.

Résumé

1. Ten samples from the same rubber were subjected for 2 hours to loads of 100, 200, etc., up to 1000 grams. Two hours after release the permanent set after 10 per cent elongation was 0.15 per cent, and after 300 per cent elongation it was 1.8 per cent. Twenty-four hours after release it had fallen to one-half to one-third of these values. After about 1 year the samples which had been elongated 100 per cent no longer showed any permanent set, so that up to this degree of elongation rubber may be regarded as completely elastic.

2. The Poisson constant was determined up to 8.7 times the initial length, and an average value of 0.490 was found.

3. The modulus of elasticity was approximately 0.102 kg. per sq. mm. at low elongations; for about 70 per cent elongation it had a minimum value of 0.086 kg. per sq. mm. and with increasing tension it increased at first slightly, then from 100 per cent elongation on it increased rapidly until shortly before rupture it reached a value of around 1000 kg. per sq. mm., *i. e.*, of the order of magnitude of the modulus of wood. Considering the fact that x-ray interferences first appear at 100 per cent elongation, this increase of the modulus of elasticity from 100 per cent on is apparently to be attributed to a highly organized state of the molecules.

4. When under tension rubber is brittle just before rupture.

The present work was carried out in the Department of Applied Mechanics and Thermodynamics in the Physical Institute of the University of Leipzig. I wish to thank my highly esteemed teacher, Dr. Schiller, for the preparation of the material used and for his assistance in the carrying out of the work. I also wish to thank Assistant Dr. Hermann for his kind advice.

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A Contribution to the Problem of the Impregnability of Cord Threads with Rubber

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A review of the different methods employed today for preparing the carcass of tires will distinguish two main principles of working:

1. The direct treatment of dry fabrics (cord fabrics, weftless cords) with raw rubber compounds either by simply applying skim coats or by combining this operation with frictioning rubber on by calendering.

2. The pre-impregnation of the fabric or weftless cord either with a rubber solution or with latex. Latterly the direct application of latex (natural rubber milk) has found more and more favor in this industry also, and it is certainly possible to use latex for impregnation, instead of rubber solutions or cements. This is evident from the practice of the natives of Brazil in making their waterproof fabrics.

The second category of processes may accordingly be divided into two subgroups: those which work with benzine rubber solutions and those which use latex. While comparatively simple tests enable us to find out with the greatest ease why the use of cord fabrics or weftless cords has other advantages over the use of closely woven fabrics, in addition to the higher degree of elasticity already referred to, it is much more difficult to decide whether it is more advantageous to use dry fabrics previously impregnated with benzine rubber solutions or fabrics that have been pre-treated with latex.

It is perfectly obvious that in a closely woven fabric, in consequence of the continual distortions to which a tire may be subjected in service, chafing effects must show themselves wherever the warp and weft threads are in contact. These chafing effects will naturally be converted into heat, which, as has been demonstrated by very simple tests, may reach quite high temperatures. It is further obvious that this development of heat must have an injurious effect, not only on the fabric itself, but also on the rubber of the skimcoats, so that the life of the tire is shortened by the destruction of the internal cohesion. This disadvantage has been in a large measure counteracted by the use of layers of weftless cord. But, as already said, it is far more difficult to decide, when loosely woven fabrics are used, whether the pre-impregnation of the different component parts of the fabric with rubber solutions or cements or with latex offers advantages over the dry treatment or not. Some firms hold the view, as practically illustrated in their patents, that pre-impregnation with rubber solution or latex is better, because this effects a better cohesion of the threads, and at the same time a more thorough penetration of the individual threads. Others maintain, however, that the dry treatment of cord fabrics is more advantageous.

In technical literature it is sometimes stated that pre-treatment with latex has special advantages because a better impregnation is attained with it than with the use of benzine-rubber solutions.

When we come to examine carefully what has been written on the problem under discussion, it is especially astonishing to find that scarcely any arguments founded

on actual experiment can be adduced in support of the multitude of theories propounded.

It therefore seems desirable, from a purely technical and scientific point of view, that the question of impregnability by the aforementioned methods should be submitted to a systematic and detailed experimental investigation. In the existing literature there are, as we have said, very few references to any such experimental research. We may mention an article by Dieterich,¹ and another by E. Grenquist.² The methods described in these two articles are almost identical. Dieterich vulcanizes the specimen to be investigated to the ebonite point, and then cuts it on the microtome, while Grenquist before proceeding to microtomy strongly over-vulcanizes the surface of the preparation by cold-curing with a solution of sulfur monochloride.

Although Dieterich's results on the whole confirm our own findings from the experiments described later on, we must still maintain, on the ground of our many years' experience, that the methods followed by these writers cannot stand up against rigorous criticism, for the phenomena to be mentioned below show that there can be no guaranty that, during the ebonite vulcanization of the outer coating or the over-vulcanization of the surface with sulfur monochloride, no changes will take place that may more or less seriously affect the final result. This criticism applies especially to the method proposed by Dieterich for investigating specimens which have not a sufficiently thick coating of rubber to admit of microtome sections being made with certainty. In such cases, Dieterich recommends embedding the specimens in thin coatings of unvulcanized compound. It must be further noted that Dieterich's proposal of embedding preparations in a saturated polysulfide solution is not free from objection, in so far as, in those parts of the fabric which are not impregnated with rubber, swellings may occur which may have a considerable influence on the final picture.

In view of such considerations, therefore, it has been our aim from the start to evolve a method which would allow of a microscopic examination of the preparations without any further previous treatment.

In brief, our method is as follows:

A. *The preparation of fabric layers or weftless cords which are enveloped in a sufficiently thick (visible) layer of rubber*, such as, for instance, fabric layers coated on both sides with or without previous impregnation, sections of finished tires, etc. The specimen to be investigated is fixed in hard-setting paraffin. When the paraffin is firmly set, it is cut into blocks in such a manner that the specimen under examination lies, as far as possible, in the middle of a block. The block is then mounted on a sliding microtome.³ When it has been set at the right height for cutting, and the upper surface has been cut smooth, the top of the block is treated with carbonic acid till it is frozen to a depth of about 200μ . The slide is then rapidly moved under the knife and a microsection of $20\text{--}30\mu$ in thickness is cut. This microsection is now spread out in tepid water and laid on a microscope slide. After the adherent moisture has been cautiously evaporated, the slide with the preparation is immersed in clean concentrated sulfuric acid. The paraffin is to a large extent destroyed through the action of the sulfuric acid, but all parts of the fabric which are not impregnated with rubber are carbonized. The rubber mass itself is stained a characteristic reddish brown color. The preparation is left for 1-2 hours in the sulfuric acid, and is then washed with clean concentrated sulfuric acid until all soluble or carbonized ingredients have disappeared. Then the preparation can either be at once subjected to microscopic examination, or be finished as a permanent preparation by embedding in Canada balsam or some similar substance.

B. The preparation of specimens which are not enveloped in a rubber coating of any considerable thickness, such as, for example, cord fabrics, weftless cords, or single threads, pre-treated with benzine solution or latex.

The specimen is laid in a 7 per cent solution of gelatin, which is then solidified by cooling. The congealed gelatin is then cut into blocks in the manner already described, and these are mounted on a freezing microtome. By means of suitable refrigerating mediums, such as carbon dioxide, the mounted gelatin block is completely frozen and a microsection is then cut. The section is laid on a microscope slide and, as above described, is subjected to the action of concentrated sulfuric acid. The gelatin in which the preparation is enveloped is hereby completely destroyed, so that, after it has been washed, the specimen is ready for examination.

Materials Examined

The following materials adapted for the solution of the main problem were subjected to investigation in the form of microsections:

1. A thread soaked in a 5% benzine-rubber solution.
2. The same thread after treatment with sulfuric acid.
3. A thread soaked in 33% ammonia latex.



Figure 1—Single Thread Soaked in a 5% Rubber Solution
Microsection

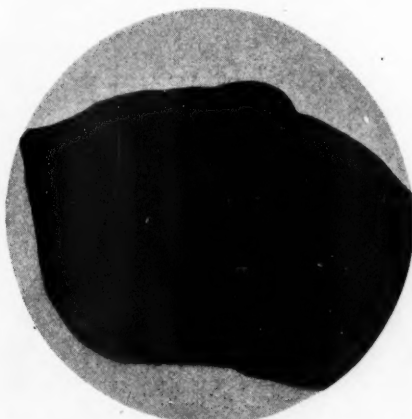


Figure 2—Single Thread Soaked in a 5% Rubber Solution—after Treatment with Sulfuric Acid
Microsection

4. The same thread after treatment with sulfuric acid.
5. Dry cord threads onto which a rubber compound had been frictioned.
6. The same weftless cord after treatment with sulfuric acid.
7. Cord fabric previously soaked in benzine-rubber solution, then covered on both sides with skim-coats by friction calender, and afterward treated with sulfuric acid.
8. Latex cord fabric coated on both sides and treated with sulfuric acid.
9. The same cord fabric as in No. 7, coated on both sides and treated with sulfuric acid after vulcanization.
10. The same cord fabric as in No. 8, coated on both sides and treated with sulfuric acid after vulcanization.
11. A dry cord fabric laid in sheets and treated with sulfuric acid after vulcanization.

In Fig. 1 we immediately recognize a thread consisting of several filaments. Figure 2 shows that the fiber remains practically unchanged after treatment with sulfuric acid, as is plainly attested by the red-brown coloring of the whole section.

In Fig. 3 the only difference from Fig. 1 is that on closer observation we notice a somewhat thicker layer of rubber on the surface of the thread. This agrees with the fact, which can be easily demonstrated by experiment, that more rubber



Figure 3—Single Thread Soaked in 33% Latex
Microsection

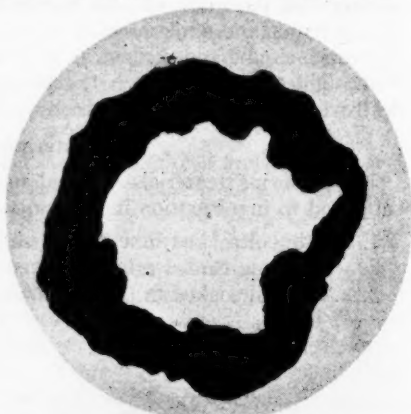


Figure 4—Single Thread Soaked in 33% Latex—
after Treatment with Sulfuric Acid
Microsection

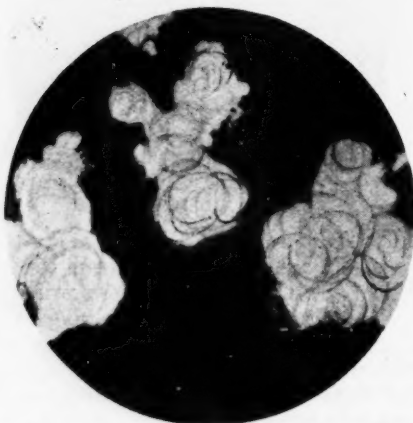


Figure 5—Dry Cord Threads onto Which Rub-
ber Compounds Have Been Frictioned
Microsection



Figure 6—Dry Cord Threads onto Which
Rubber Compounds Have Been Frictioned—
after Treatment with Sulfuric Acid
Microsection

is taken up by a thread which has been soaked in latex than by one soaked in benzine-rubber solution.

Figure 4, on the other hand, differs characteristically from Fig. 2. We see that the sulfuric acid treatment of the thread previously soaked in latex has caused almost total destruction of the fiber, so that nothing but the outside covering is visible. This photograph confirms the fact that, as was to be expected from purely theoretical considerations, a thorough impregnation can never be attained

by treatment with latex, but that the rubber present in the latex will merely be deposited on the surface. The reason for this is easily explainable by the circumstance that the rubber hydrocarbon contained in latex is present in the form of an endless number of minute particles, whose average diameter is estimated at $1-2\mu$. When we consider that the capillary interstices of the fibrous tissue are considerably smaller than these particles, it follows logically that the latex particles cannot penetrate into the interior of the thread, but that in the best of cases the aqueous dispersing medium of the latex is absorbed into the core.

This fact we were able to confirm experimentally in the course of our investigations on the degree of swelling of the fiber.

Figure 5 reproduces the microscopic picture of sheets (skim-coats) obtained by frictioning rubber on to weftless cord.

Figure 6 shows the same sheets after treatment with sulfuric acid. We see here again that there has been no penetration of the rubber into the fiber, as this has been completely dissolved out by the action of the sulfuric acid. This was

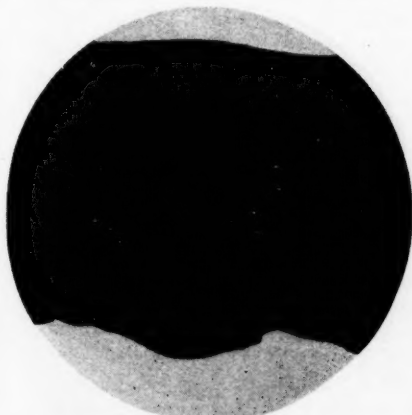


Figure 7—Cord Fabric First Soaked in Rubber Solution and Then Covered on Both Sides with Skim-Coats by Frictioning—after Treatment with Sulfuric Acid

Microsection

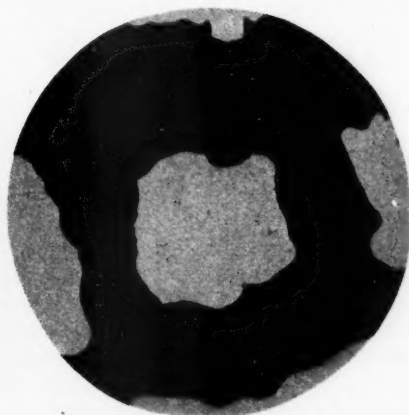


Figure 8—Cord Fabric First Soaked in Latex and Then Covered on Both Sides with Skim-Coats—after Treatment with Sulfuric Acid

Microsection

also to be expected theoretically, as a far more plastic mixture would be necessary for impregnation by this process, quite apart from the fact that, in order to obtain complete penetration, pressures are required which would cause the complete destruction of the fabric.

Figure 7 shows a layer obtained by coating with rubber a cord layer which has been previously soaked in benzene-rubber solution. This picture is therefore in a certain sense comparable with Fig. 2. Here, too, we see that proof is given by the sulfuric acid treatment that the rubber has at this stage already penetrated completely into the fiber.

Figure 8 reproduces the microscopic picture of a layer produced by coating cord threads previously soaked in latex. We notice here, as in Fig. 4, a total disappearance of the fiber. We can further notice that there is a sharp line of demarcation between the latex layer and the superimposed sheet.

Earlier investigations concerning the vulcanization of rubber carried out by us by microscopic methods⁴ established the fact that during the process of vulcanization rubber exhibits a more or less pronounced flow effect, varying in degree

according to the physical condition of the rubber and the actual compound used. In view of this fact it seemed important, for a complete solution of the problem before us, that the impregnability of threads which have undergone different forms of pre-treatment should also be studied after vulcanization, for it was to be assumed that the flow effect to be expected in certain preparations would cause considerable differences in the degree of impregnation.

We here merely quote a few facts resulting from these earlier researches which are of importance for what has to follow:

1. Rubber which has undergone no mechanical treatment before vulcanization ("unbroken" rubber, such as latex, for example) exhibits scarcely any flow effect at all.
2. Rubber which has been pre-kneaded by mastication exhibits flow effect in proportion to the degree of mastication.
3. Rubber obtained by evaporation of benzine-rubber solution exhibits flow effect to a degree practically equal to that of strongly masticated raw rubber.

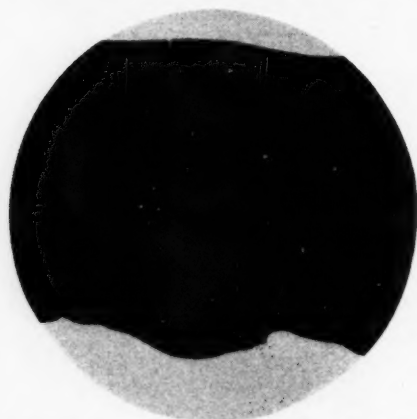


Figure 9—Cord Fabric First Soaked in Rubber Solution and Then Covered on Both Sides and Vulcanized—after Treatment with Sulfuric Acid

Microsection

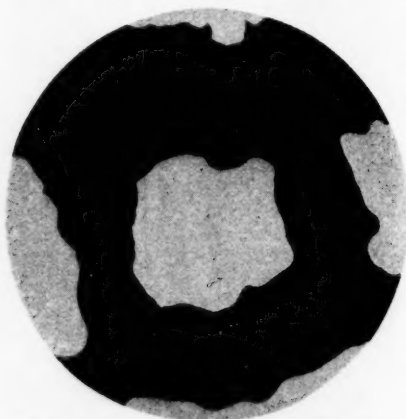


Figure 10—Cord Fabric First Soaked in Latex and Then Covered on Both Sides and Vulcanized—after Treatment with Sulfuric Acid

Microsection

4. The addition of accelerators diminishes the extent of flow and especially the time of flow, and the greater the strength of the accelerator, the greater this effect.

Figure 9 reproduces the sheet already shown in Fig. 7 after it has been vulcanized and subsequently treated with sulfuric acid. As is to be expected from what has already been said, no characteristic change has taken place through vulcanization; closer examination only enables us to establish the fact that the rubber impregnation has become more uniform. We can further see that during the vulcanizing process a complete fusion of the outer impregnation layer with the superimposed sheets has taken place.

A marked difference from this is presented by a vulcanized sheet consisting of threads soaked in latex and skim-coated, and then treated with sulfuric acid, as can be seen in Fig. 10. (This figure may be compared with Fig. 8.) We see here that no change in the degree of impregnation has resulted from vulcanization, so that the thread can also be completely dissolved out after vulcanization. We further notice, in contrast to Fig. 9, that no fusion has taken place between the

outer latex layer and the skim-coat. This phenomenon is due, as explained above, to the circumstance that it is a question here of unbroken rubber, so that in the absence of flow neither a further penetration of rubber into the thread nor a fusion with the pre-masticated skim-coat is to be expected. The correctness of our observations in our earlier investigations is demonstrated with remarkable clearness in Fig. 11, which shows a dry weftless cord embedded in rubber sheets as it appears after vulcanization and treatment with sulfuric acid. This figure is therefore to be compared with Fig. 5. We see from it that, in consequence of the flow of the rubber which takes place during the vulcanizing process, an almost complete penetration of the thread has resulted, since the treatment with sulfuric acid has caused no destruction of the fiber tissue, and the whole of the thread has assumed the characteristic reddish brown color.

The results of our investigation may be briefly summed up as follows:

A fabric previously soaked in a benzene-rubber solution is already completely impregnated with rubber before vulcanization, whereas a fabric

soaked in latex is only covered with an external coating of rubber even after vulcanization. When non-treated threads are embedded in rubber sheets, or rubber compounds are frictioned onto dry fabrics, there is no impregnation, previous to vulcanization, but impregnation takes place in a high degree during the process of vulcanization in consequence of the flow of the rubber.

With the establishment of these facts, we consider that we have proved that the degree to which weftless cords can be impregnated in a vulcanized state depends not so much on whether the fabric has been previously treated or not, but solely on the physical condition of the rubber used. With rubber in the form of a benzene solution, or a solution in any other solvent, a more or less perfect impregnation may be reckoned on, whereas if latex is used, merely an external coating of the thread and no impregnation is the result.

The question as to whether cord fabrics and weftless cords prepared with benzene-rubber solutions or those prepared with latex can claim superiority in regard to strength, elasticity, durability, etc., is not decided by the results of the investigations here described, nor, indeed, did the solution of this question lie within the purpose of this article.

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- ¹ *Ind. Eng. Chem., Anal. Ed.*, **1930**, 102.
- ² *Ibid.*, **1928**, 1073; Green, *Ind. Eng. Chem.*, **1921**, 1130; Steele, *Ind. Eng. Chem., Anal. Ed.*, **1930**, 421.
- ³ A Leitz large sliding microtome was used.
- ⁴ Hauser and Hünemörder, *Caoutchouc & gutta-percha*, **1928**, 14146; Hauser, *Colloid Symposium Monograph*, **1928**, 207.



Figure 11—Dry Cord Layer onto Which Skim-Coats Have Been Frictioned, afterward Vulcanized and Treated with Sulfuric acid
Microsection

Laboratory Rubber Testing. Its Relation to Service

R. P. Dinsmore

The rubber technologist of today is situated in one of the most competitive and rapidly changing industries. He is faced with the necessity of producing an important structural material of varied forms and compositions which must constantly be modified to meet new requirements of economy and service. He must be prepared to furnish, upon demand, rubber in new forms and colors, which will serve successfully in increasingly exacting conditions of temperature, flexing, abrasion, and more often than not in conjunction with a totally dissimilar material. To anticipate these demands he must engage in a ceaseless search for new and more effective materials, both in his own research laboratory and amid the countless new natural and synthetic materials which appear on the market.

The time has passed when long periods of preparation can be utilized for the development of new compounds and products. The pressure of modern industrial development constantly brings about new conditions which must be met when they arise. The success with which the technologist fulfils these obligations depends in large measure upon his ability to predict the behavior of his materials under the conditions of service. When, as is often the case, his knowledge of both materials and service conditions is limited, results frequently fall far short of expectations.

Even when a satisfactory product is established for a time, the rubber chemist has a problem in controlling the uniformity of his product. This has frequently been discussed in many of its phases. It is sufficient to remind ourselves that, in control testing, primary specifications, that is, specifications which cover the factors governing service performance, are the only entirely reliable kind. Unfortunately, our limited knowledge allows us to write few such specifications for rubber testing. The other type of specification is effective only so long as the method of manufacture of the material is uniform and constant. This is not true of rubber, our basic raw material.

These preliminary remarks are intended to emphasize the importance to the rubber technologist of reliable methods of laboratory testing, which can, to some known degree at least, be related to service performance. It is obvious that dependence upon service-testing of materials is an economic waste, and one that offers little promise of keeping pace with the continuous demand for new products and the necessity of evaluating so many new materials. Only the larger corporations can afford to carry on large-scale service tests, and these only on their major products. Factory control by such methods is naturally out of the question. Then too, if the art of rubber goods manufacture is ever to approach a science, it must be by some faster and more certain method of collecting data than is afforded by service performance. We are faced, then, with the need for laboratory tests which can be interpreted in terms of performance, and it may be helpful to ask how nearly the satisfaction of that requirement is approached.

It has been pointed out elsewhere that, since almost all rubber products are vulcanized, determination of the state of vulcanization is a vital factor. Un-

doubtedly the present lack of correlation between service and laboratory testing is responsible for most of the disagreement in this matter.

The desperate need of the rubber technologist for some rapid means of controlling his products has brought about a number of laboratory tests. The two oldest methods, probably imported from the metal industries, are the slow-speed stress-strain test and the hardness gage. Specific gravity and combined sulfur determinations have also long been in use. In recent years a considerable number of devices have made their appearance. Abrasion machines of varied construction, fatigue testers, impact instruments, tear testers, various modifications of the stress-strain test, and semi- and full-size product tests have been offered to the bewildered technologist. In most part they have been ignored or have fallen into disuse.

There is a certain comforting satisfaction in reducing one's observations to numerical quantities. The modern rubber technologist is prone to look with a certain patronizing contempt upon the methods of his less scientific predecessors. Yet the most experienced know and rather reluctantly will admit that even their most prized laboratory tests cannot be reliably and infallibly interpreted in terms of service performance. However, this fact is not always kept clearly in mind. Many errors in judgment occur because the quantitative figures of the laboratory lull the mind into a false confidence in their authority which experience does not justify. This is not an argument against inadequate laboratory tests if they are the best thing available, but it is a reminder that they must constantly be reappraised and kept in their true proportion.

A few examples of the unreliability of laboratory methods and a discussion of the uses to which they are put will serve to make this situation clear.

RUBBER COMPARISON IN FIRST-GRADE TREAD STOCK

Test	Load at Elongation		Tensile, Kg. per Sq. Cm.	Ultimate Elongation, %	Abrasion Resistance		Resistance to Road- Wear, %
	300% Kg. per Sq. Cm.	500% Kg. per Sq. Cm.			Angle Machine, %	Grasselli Machine, %	
Control	70	182	300	660	100	100	100
L. S. rubber and stearic acid	77	188	294	665	76	91	75
L. S. rubber. No stearic acid	85	200	300	645	70	63	88.5

This table shows a comparison of standard rubber with sprayed-latex rubber in a high-grade tread stock. The stress-strain data indicate superiority, while the abrasion figures more nearly predict the service results. It is interesting to note that the absence of stearic acid in this case improves the performance to a marked degree.

ACCELERATOR COMPARISON IN FIRST-GRADE TREAD STOCK

Stock No.	Parts by Weight per 100 Rubber			Load at Elongation		Tensile, Kg. per Sq. Cm.	Ultimate Elongation, %	Abrasion Resistance		Resistance to Road- Wear, %
	S	Mercapto- benzo- thiazole	Di- phenyl- guanidine	300% Kg. per Sq. Cm.	500% Kg. per Sq. Cm.			Angle Machine, %	Grasselli Machine, %	
1	2.80	1.90	0	68	176	314	700	100	100	100
2	3.25	0.50	0.50	85	182	316	690	98	79	79
3	3.00	0.50	0.50	78	190	316	675	107	82	82
4	2.80	0.45	0.45	80	192	312	660	91	90	90
5	2.80	0.50	0.50	76	192	312	660	100	79	79

This table gives some striking examples of the misleading results of both stress-strain and abrasion data. In all cases the stress-strain data are superior. In

two cases abrasion figures indicate equality with the standard, in one case distinct superiority, and in the remaining case decided inferiority. The road-wear in all cases was well below standard, and in only one case would any of the physical data have predicted this result.

FATTY ACID COMPARISON IN FIRST-GRADE TREAD STOCK

Stock No.	Load at Elongation		Tensile, Kg. per Sq. Cm.	Ultimate Elongation, %	Abrasion Resistance		Resistance to Road-Wear, %
	300% Kg. per	500% Sq. Cm.			Angle Machine, %	Grasselli Machine, %	
1	88	218	320	620	100	100	100
2	89	220	327	625	95	99	93
3	80	191	315	685	88	89	101

No. 1 contains stearic acid and is the control.

No. 2 contains substitute from vegetable oils.

No. 3 contains mixed acids of unknown composition.

This is an interesting comparison of fatty acids, which shows two different results. In one case (No. 2) the physical data are substantially equal to the control, but the resistance to road-wear is poorer. For the other stock (No. 3) the physical data are distinctly inferior, whereas the resistance to road-wear is equal to the control.

COMPARISON OF CARBON BLACK SAMPLES IN TREADS CONTAINING 23 VOLUMES

Black	Load at Elongation		Tensile, Kg. per Sq. Cm.	Ultimate Elongation, %	Abrasion Resistance		Flexing Resistance, %	Resistance to Road-Wear, %
	300% Kg. per	500% Sq. Cm.			Angle Machine, %	Grasselli Machine, %		
Standard	75	189	316	675	100	100	100	100
Ultra-micronex	83	204	308	640	110	98	97	92
Carbacell	80	201	314	650	114	109	80	95

Here, again, high physical properties are obtained with two different blacks, which yield inferior road-wear. Certainly no one would have expected this result from the laboratory tests. On the other hand, experience with blacks giving low stress-strain and abrasion figures and which give poor road performance is common. Thus there is a lack of correlation between laboratory and service tests, and with the type of test as now made correlation is impossible.

These illustrations show clearly that stress-strain and abrasion data are not reliable guides to service performance. Instances have been cited which indicate that whether the physical data are inferior, equal, or superior, discrepancies in performance may result. Discrepancies between natural and accelerated aging have been discussed elsewhere, and other laboratory methods might be held up for critical examination. However, stress-strain, abrasion, and aging tests are most commonly referred to in the literature, and are as a matter of fact the backbone of today's laboratory testing. As previously stated, there is no intention of attempting to demonstrate that there is no value in laboratory testing. It is desired merely to emphasize the fact that the old standard methods are inadequate and hence likely to be misleading.

Whether as manufacturers of raw materials, research workers, or control chemists, it must be recognized that our laboratory tools are antiquated and unreliable. If it is desired to control the manufacture of raw materials for rubber products, to control the products themselves, or to evaluate new materials, the technologist is faced with the alternatives of faulty judgment or the well-nigh prohibitive use of slow and expensive service testing.

The question naturally arises as to what is to be done about the situation. It is clear that the need for new tests and the modification of present ones has been recognized for some time. The variety of devices, referred to earlier, is proof of this fact. The modifications of our stress-strain methods which involve higher temperatures and more accurate determination of stress at low elongations are a



Figure 1

move in this direction, and have been described in the literature by others. The obvious fact remains, however, that all such innovations are of mere academic interest until they have been effectively correlated with service performance.

Certain facts suggest avenues of approach to this problem. In many types of service the rubber is flexed rapidly, and because of its low conductivity it rises

in temperature. Obviously, data obtained under essentially isothermal conditions at low speeds may be expected to be misleading. Rubber is partly plastic and partly elastic. Slow deformation emphasizes its plastic properties, while fast deformation develops more elasticity. High temperatures appear to increase the plasticity effect at slow speeds and elasticity effect at high speeds. Of course the degree of vulcanization is an important factor also. It is probable that this dual nature of rubber is equally important in stress-strain, fatigue, and adhesion tests. It may be a factor in abrasion testing also. In studying abrasive wear, the direction and degree of deformation undoubtedly strongly influence abrasive loss and any attendant fatigue-cracking. These factors cannot be ignored in the design of laboratory tests. A hint as to possible methods for studying this matter is shown in the following illustrations.

Figure 1 shows an arrangement by means of which a tire may be pressed against a vertical glass plate, thereby bringing about a deformed tire surface similar to that of a loaded tire in contact with the ground. The appearance of the tread may be observed through the plate and observation may be aided by cross-hatching of the tread surface. The inner surface of the glass may be lined in order to aid in the estimation of tread distortion.

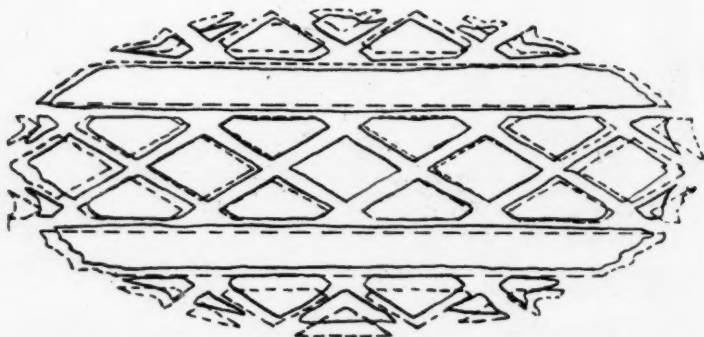


Figure 2—Goodyear Tire on Flat Plate

1700 lbs. load. 36 lbs. inflation. ——— Print on plate. - - - Print on tire.

Figure 2 shows a copy of a print made by loading a tire against a plane surface with carbon paper interposed. This indicates the distortion of the non-skid surface, without of course giving any indication of the contour changes of the sides of the non-skid and the groove bases.

Figure 3 is an interesting picture of point movement on the tread surface. The record was made by sanding a polished metal surface, carefully pressing a tire against it, and slowly loading the tire. The scratches on the metal surface correspond to point movement of the superimposed tread surface.

This leads to the thought that more effective laboratory methods may result from careful mechanical analysis of the behavior of rubber products in service. Rubber chemists have naturally failed to appreciate the full value of mechanical studies, but they must turn to the physicist for aid in their difficulties. A sound theoretical basis may serve materially to shorten the tedious search for laboratory and service correlation. Certainly the haphazard development of new tests must lead but slowly to progress.

In closing it may be said that it is hoped that rubber technologists will awake to the serious need for the solution of these problems. The industry has no need to be ashamed of the brilliant contributions to knowledge made by its research

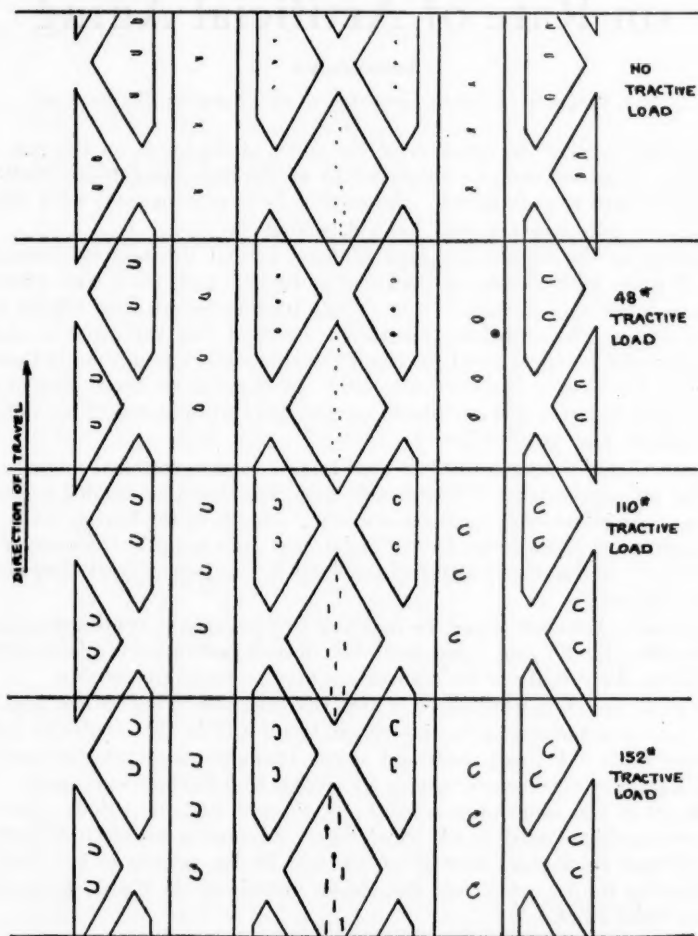


Figure 3—Movement of Tread Contact Area of a Goodyear Tire
Inflation: 36 lb. per sq. in. 1400 lb. load = 1.18 in. deflection.

chemists. Yet their efforts cannot reach proper fruition unless supplemented by effective and rapid laboratory criteria. There is no desideratum of greater scientific and economic importance to all connected with this industry, or one upon which more harmonious coöperation may be secured.

The Effect of Specimen Thickness on Rate of Artificial Aging

Anonymous

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From time to time the question of the effect of thickness on the rate of deterioration of rubber samples subjected to accelerated aging tests, particularly the oxygen-bomb test, is raised. Apparently little experimental work has been done, and no satisfactory answer has yet been given.

According to the well-known laws of mass action, the rate of deterioration should slow up with increasing thickness of rubber, and one might expect thin articles to deteriorate further, in a given bomb-aging period, than similar articles of heavier gage. Nevertheless, it is tacitly assumed that variations in thickness have practically no effect—and for small variations this assumption is reasonable considering the oxygen concentration used; or possibly no assumption is made, and the aging tests are just performed mechanically without regard for theoretical considerations and possibilities.

The fact that the oxygen-bomb is used largely for comparing the aging quality of similar articles, usually of comparable gage, has doubtless tended to keep the question of the influence of thickness dormant. Again, in the testing of laboratory compounds, most laboratories have standardized on a uniform thickness of cured slabs (0.075"), so that the question of thickness in this type of work does not come into the picture.

Occasionally, however, it may be desirable to compare the bomb-aging behavior of articles of quite different types, and when in such cases there is a large difference in thickness, the validity of the comparison may be called in question.

In order to ascertain what effect, if any, the thickness of the rubber might have on the rate of deterioration in the oxygen-bomb and in the oven, the following tests were made. A tread stock and a wire insulation were selected, and cured slabs in a series of thicknesses varying from 0.025 to 0.150 inch were made. These were placed in the oxygen-bomb for 2-, 4-, 8-, and 10-hour periods, after which they were machine-tested in the usual way. Another series of cured slabs with three different thicknesses were given 14- and 28-day periods in the Geer oven. The following results, which are also shown graphically in Fig. 1, were obtained from the tread stock.

Remarks.—It should be noted that the slabs of heaviest gage are six times as thick as the lightest slabs. Notwithstanding this large difference in thickness, the deterioration appears to proceed at about the same rate in both cases, as also in those of intermediate gage. The graphs of Fig. 1 show the mean tensile strength of the two cures plotted against specimen thickness, and they demonstrate well this equality of rate of deterioration in the oxygen-bomb.

The tensile-thickness curves are all practically straight horizontal lines. If increasing thickness had the effect of slowing up the rate of deterioration, the curves would slope upward. As a matter of fact they all have a very slight downward tendency. This may be explained by the fact that, as thickness increases, the tendency of the died specimens to have concave sides increases; the greater the concavity, the further does the cross-sectional area depart from the true value,

Pale crepe	50
Smoked sheets	50
Stearic acid	4
Pine tar	2
Age-rite powder (phenyl- β -naphthylamine)	2
Zinc oxide	1
Gas black	5
Sulfur	40
Captax (mercaptobenzothiazole)	3
Total	1
	156

**Press Cures at
30 Lbs. Steam
(274° F.)**

[illegible]

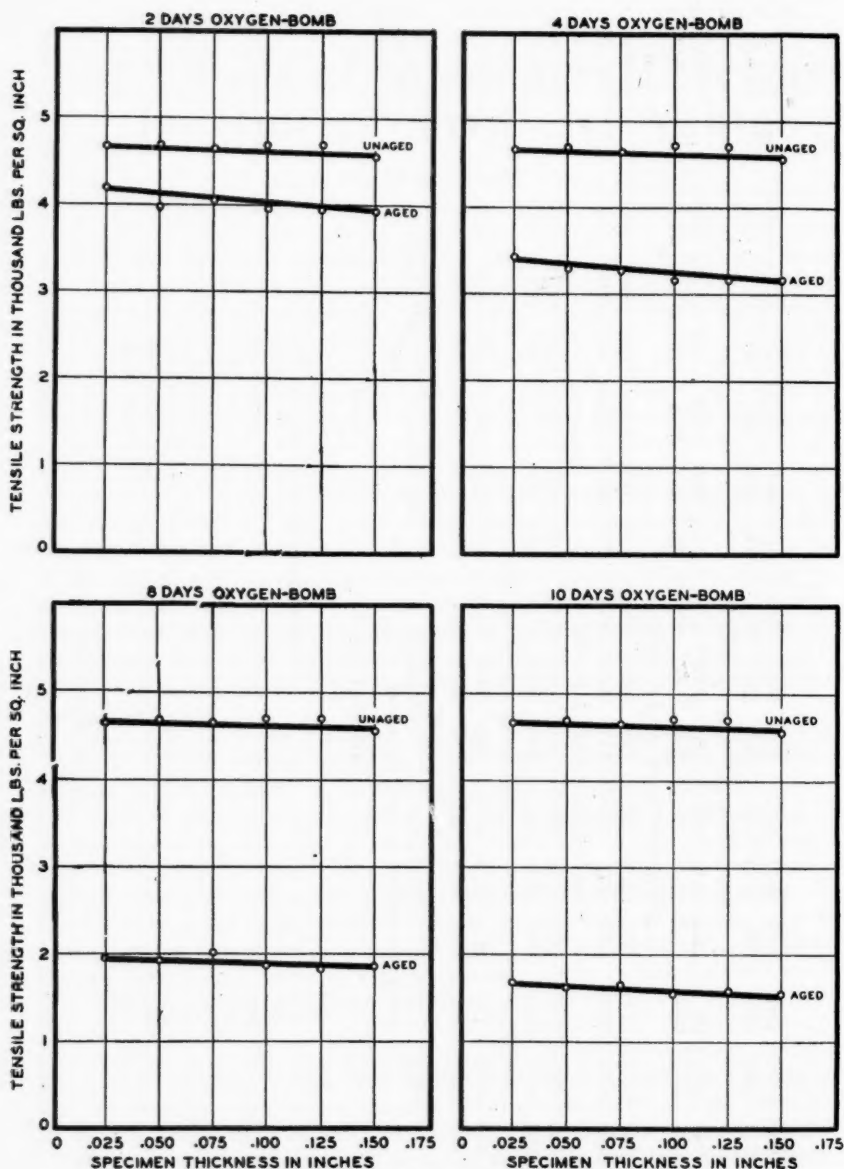


Figure 1—Tread Stock in Oxygen-Bomb

assuming the sides to be straight, and the lower the tensile values. A slight lag in the cure with increasing gage may also offer an explanation.

Remarks.—The data given above and graphically in Fig. 2 show the effect of thickness on the bomb-aging behavior of a "superaging" wire insulation compound. The behavior is exactly comparable, as far as thickness is concerned, with that of

AGING IN OXYGEN-BOMB Wire Insulation Stock

Pale crepe	50
Smoked sheets	50
Stearic acid	0.5
Age-rite powder (phenyl-β-naphthylamine)	1.5
Paraffin	3
Zinc oxide	42
Gilders whiting	127
P-33 carbon black	0.7
Altax (benzothiazyl disulfide)	0.35
Tuads (tetramethylthiourea disulfide)	1.50
Telloy (tellurium)	0.50
Total	277.05

Physical Properties

Press Cures at 24 Lbs. Steam (265° F.)	Stress at 300%—Tensile Strength—% Elongation at Break							
	0.025 Gage	0.050 Gage	0.075 Gage	0.100 Gage	0.125 Gage	0.150 Gage	0.175 Gage	0.200 Gage
30 min.	585	1890	515	565	1890	530	615	1870
45 min.	615	2040	535	580	1925	535	635	1955
30 min.	705	1880	500	715	1835	500	740	1840
45 min.	685	1780	500	720	1840	495	735	1855
30 min.	790	1690	475	735	1800	490	800	1790
45 min.	745	1820	480	735	1780	480	810	1790
30 min.	705	1650	475	720	1575	470	770	1650
45 min.	730	1570	470	740	1565	480	770	1680
30 min.	705	1610	470	750	1570	465	750	1550
45 min.	695	1480	470	725	1605	485	785	1550

Before Aging

Aged 5 Days in Oxygen-Bomb at 70° C. and 300 Lbs. Pressure

Aged 10 Days in Oxygen-Bomb

Aged 15 Days in Oxygen-Bomb

Aged 20 Days in Oxygen-Bomb

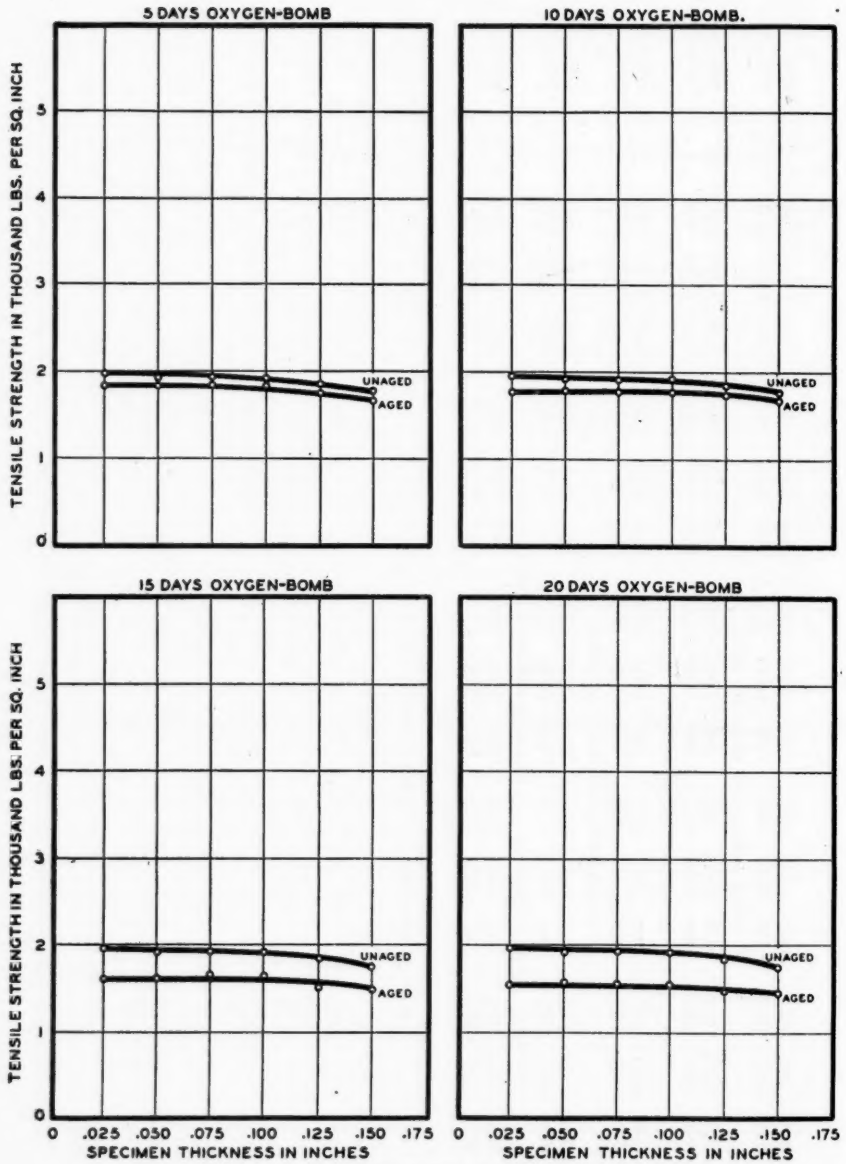
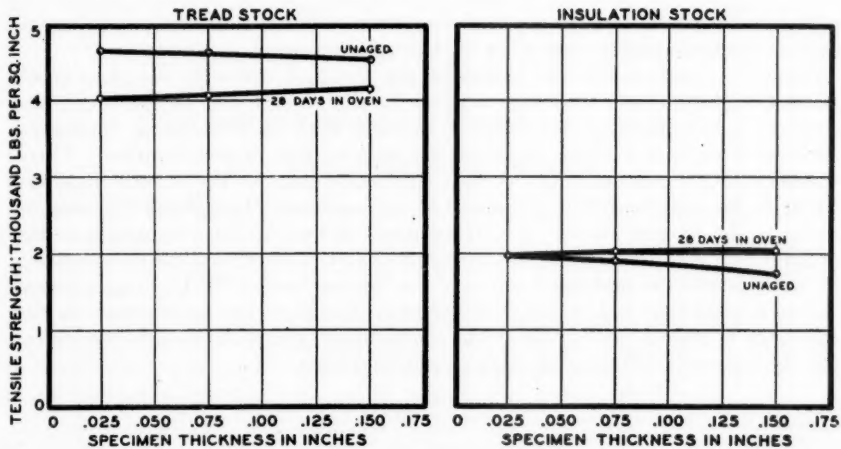


Figure 2—Wire Insulation Stock in Oxygen-Bomb

the tread stock shown previously; the tensile-thickness curves are in each case practically straight horizontal lines.

The aging periods used for the insulating stock were longer because this is a far more resistant compound than the tread stock.

The conclusion to be drawn from these experiments is, therefore, that for the range of gages shown—and it comprises those most likely to occur in commercial



work—the thickness of the specimen has no physically measurable influence on the rate of deterioration of rubber samples in the oxygen-bomb. The explanation probably is that the permeability of rubber to oxygen under the high pressure of 300 pounds per square inch is such that the concentration of oxygen is maintained uniform and equal throughout the mass of the specimen during the bomb-aging period.

Figure 3

AGING IN GEER OVEN
Tread Stock, Physical Properties
 Stress at 300%—Tensile Strength—% Elongation at Break
 0.025 Gage 0.075 Gage 0.150 Gage

<i>Before Aging</i>									
30 min. at 274° F.	850	4540	680	775	4420	690	820	4520	69
45 min. at 274° F.	1070	4800	630	1090	4860	665	1110	4540	635
<i>Aged 14 Days in Geer Oven at 70° C.</i>									
30 min. at 274° F.	1280	4350	575	1270	4540	610	1335	4510	625
45 min. at 274° F.	1640	4630	550	1640	4460	570	1740	4620	600
<i>Aged 28 Days in Geer Oven</i>									
30 min. at 274° F.	1335	3980	550	1340	3980	585	1430	4250	600
45 min. at 274° F.	1780	4070	515	1710	4100	540	1800	4080	540

Wire Insulation Stock

<i>Before Aging</i>									
30 min. at 265° F.	585	1890	515	615	1870	520	560	1685	525
45 min. at 265° F.	615	2040	535	635	1955	525	635	1820	510
<i>Aged 14 Days in Geer Oven</i>									
30 min. at 265° F.	735	1960	490	800	2170	510	855	2220	520
45 min. at 265° F.	830	2270	490	820	2170	505	810	2110	510
<i>Aged 28 Days in Geer Oven</i>									
30 min. at 265° F.	735	2010	470	760	2120	500	855	2130	495
45 min. at 265° F.	740	1910	465	775	1990	485	780	2110	500

Remarks.—The data above show the effect of three different specimen thicknesses on both tread and insulation compounds when aged in the Geer oven.

For all practical purposes, the effect of thickness, within the range tested, is as negligible for the Geer oven test as it is for the oxygen-bomb test, the tensile-thickness curves being again practically horizontal lines.

The wire insulation compound shows no deterioration but, instead, an improvement in physical quality even after 28 days of oven aging.

It will be observed that the 28-day tensile-thickness curve for the tread stock shows a slight upward tendency, whereas in the case of the oxygen-bomb the tendency is downward. This seems to indicate that, in oven aging, increasing thickness does have a slight retarding influence on rate of deterioration. Theoretically, the retardation ought to be considerable because the oxygen must act chiefly at the surface of the specimen, and not uniformly throughout the mass, as occurs in the oxygen bomb. If it is assumed, however, that the oxygen of the air plays only a secondary part in the oven test and, further, that the deterioration is mainly due to the prolonged action of the temperature of 70° C., then a reason for the negligible retarding effect of specimen thickness on deterioration in the Geer oven is plainly perceptible. The temperature, if not the oxygen concentration, is uniformly effective throughout the specimen.

Factory Mixed Stocks Method for Maintaining Uniformity

J. E. McCarty and Edward Cousins

Close control of milled rubber stocks is important to all rubber manufacturers. The present system developed by the authors is based on the determination of loads for given elongations, using a modified dumbbell strip. An outline of the testing routine follows.

Samples from every milled or Banbury mixed batch come to the control laboratory, each sample being accompanied by an identifying card which contains provision for recording all data of interest on that particular batch. As the samples arrive, they are weighed on a laboratory scale to give a definite volume.

The molds used for curing contain 32 cavities, each with overflow channels; the cavities are numbered to permit identification of the samples. Each cavity is 1.25 inches (3.18 cm.) by 2.5 inches (6.35 cm.) by 0.125 inch (0.32 cm.). The samples are placed in the hot mold, each in its appropriate cavity, and given a short cure at 320° F. The pieces are then removed and cut out with a die to give a dumbbell strip of the dimensions given in Fig. 1. The die is open at the ends but is long enough to overlap the edges of the small slabs, thereby facilitating the separation of the test strips from the remainder of the slab.

Figure 2 gives a view of the machine used in testing these dumbbell strips. At the lower right of the machine are shown the die and the tray containing pieces to be tested, with the accompanying identification cards. The lower jaw A of the machine is pulled down by the link chain through a sprocket and throw-in clutch arrangement. The upper jaw B pulls on the pendulum through the cable. As the test piece stretches, the jaws separate, and at a predetermined amount of stretch the contacts break, stopping the motor instantly through a dynamic brake. The operator releases the clutch by taking his foot off a pedal; a counterweight returns the jaw up the slide and, through the contacts meeting again, the motor starts up. The pendulum is held by the pawls with the pointer giving the reading. The scale is arbitrarily divided into divisions in equal lengths. It has been carefully calibrated in terms of pounds. The allowable variation for each compound is calculated, and the results translated into scale divisions. These readings are given to the operator as the limits for each sample of that compound.

The jaws of the testing machine are like shallow boxes with three sides. In the center of the short side a groove is cut, $\frac{1}{4}$ inch (0.64 cm.) wide and extending to the bottom of the box. The inside face of this side is shaped approximately to that of the shoulders of the test piece. A partial top is formed on this end of the box by two plates separated by the width of the groove and extending back about $\frac{5}{8}$ inch (1.59 cm.). This distance between the plates and the bottom of the box is slightly greater than the thickness of the test piece. Thus there is formed a sleeve for the broad end of the test piece, the narrow part slipping in between the two top plates and through the groove on the short side. When stretched, very nearly all of the force exerted by the piece against the jaw is by the

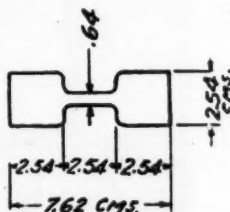


Figure 1—Sketch of Test Piece

shoulders pressing against the short side of the box. The upper jaw fits very loosely on the slide to eliminate all binding.

Discussion of Machine

Beginning with the machine used, repeated tests with dead loads showed load recording mechanism responsive to 0.1 pound (50 g.) or less. Comparison tests were made with the type of jaws and test piece used on this machine against those used in the standard procedure. The variation occurring between the different strips of each series are compared in the following table. The variation under the new procedure is expressed as a percentage of the variation occurring under the standard procedure.

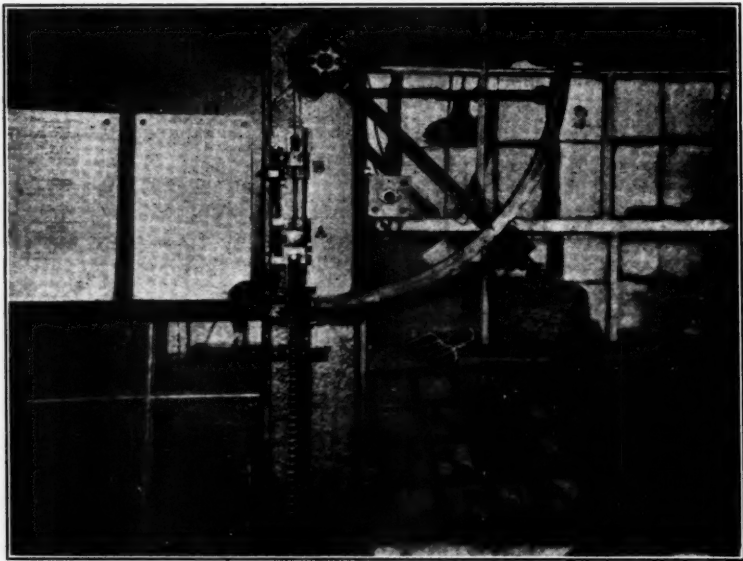


Figure 2—Machine for Testing Dumbbell Strips

	% Variation
Airbag stock	114
Solid tire stock	33
Carcass stock	50
Tread stock	50
Tread stock	100
Tube stock	53

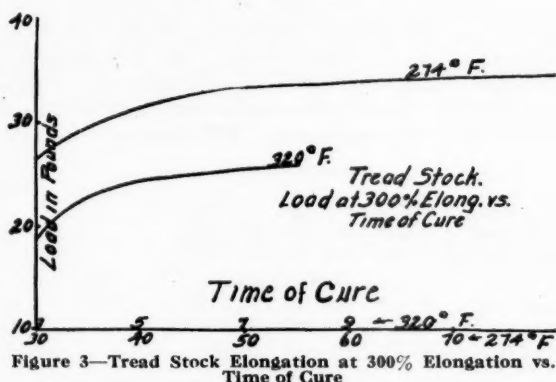
These results point to the conclusion that variation between two strips of identical composition will be no more than the variation obtained by the standard procedure.

Method of Curing

It will be noted in the outline of the procedure that the test pieces were not gaged for thickness. Check tests, made with each cavity filled with the same stocks, showed that the maximum variation in thickness in the constricted part was 3 per cent, and in tests run on the pieces, variation in load did not follow the

variation in thickness. Omission of gaging is justified, especially when the saving in time is considered.

In control work, shortness of cure is essential. Curing at 320° F. gives well set-up stocks in a few minutes; the rate of cure is about 5 times as fast as at 274°. Note Fig. 3. Samples were given such cures to avoid that portion of the curing curve where stocks are so undercured as to give very inconsistent results and at the same time escape that part of the curve where the slope is so little as to make the load-stretch relation insensitive to differences in curing rates. To avoid delay, however, the range of curing periods must be limited in number; we find two, 5 minutes at 320° and 8 minutes at 320°, satisfactory. Time and temperature of cure are matters of individual preference and necessity.



Treatment of the Sample

Samples of various stocks were taken directly from the mixers, part of each sample was chilled, and the other part maintained at an elevated temperature. After being kept in this fashion for about 15 minutes, the samples were cured, cut out, and put into a chilled or heated compartment immediately. Here they were kept for different intervals up to 15 minutes before testing. The table below gives results obtained for a carcass stock treated according to this procedure:

	Pounds Pull	
	Stock Kept Warm before Curing	Stock Kept Cold before Curing
Tested as soon as died out	9 1/4	9 1/4
Plus 5 min. in warm liner	8 1/2	8 3/4
Plus 5 min. in cold box	9	9 1/4
Plus 10 min. in warm liner	8 1/4	8 3/4
Plus 10 min. in cold box	9	9 1/4
Plus 15 min. in warm liner	8 3/4	8 3/4
Plus 15 min. in cold box	10	10 1/4

We found that no matter what the subsequent history, heating or cooling the samples before cure had no effect. Keeping the samples warm after curing resulted in little lower readings than were obtained with the pieces tested directly after being cut out. Cooling the samples after curing had a slight tendency to increase the readings. Moreover, cooling various samples in water for a brief period had no effect on the readings.

We may conclude that cooling the test pieces for a uniform time at a uniform temperature will give the best results. About four minutes are required from the time the pieces are removed from the mold until they are ready for test. The pieces are well cooled by this time, or at least at the end of an additional two- or three-minute period. The temperature of the pieces is indicated rather well by touching it to the cheek. Our experiments show that no serious variations due to differences in cooling will occur in the routine test. The factor of cooling is essential to all quick tests and is amenable to regulation in this method to the same extent as in any other.

Consistency of Routine Tests

In the foregoing, an attempt has been made to determine the effect on results of different factors entering the procedure. In a test of this kind it is important to know whether the test will remain consistent—whether checks on batches six months hence will agree with those made today. For this purpose averages were made of readings taken during a day's run on some particular stock and this work repeated at long intervals. Twenty-five stocks were dealt with in this way, and the agreements were found very satisfactory. Following are some examples:

Carcass Stock		Pounds Pull
Average reading of day's run Jan. 15, 1931		$7\frac{3}{4}$
Average reading of day's run Feb. 18, 1931		$7\frac{3}{4}$
Average reading of day's run Apr. 29, 1931		$7\frac{3}{4}$
Tube Stock		
Average reading of day's run Jan. 15, 1931		10
Average reading of day's run Feb. 20, 1931		10
Average reading of day's run May 8, 1931		$9\frac{3}{4}$
Tread Stock		
Average reading of day's run Mar. 4, 1931		$18\frac{1}{4}$
Average reading of day's run Mar. 31, 1931		$18\frac{1}{2}$
Average reading of day's run Apr. 27, 1931		$17\frac{3}{4}$

It is essential in this type of test that any important variation in the stock be easily detected. The following experiments throw light on this:

- (a) Stock with 50% of sulfur left out
- (b) Stock with 50% of accelerator left out
- (c) Stock (standard)
- (d) Stock with 50% excess sulfur added
- (e) Stock with 50% excess accelerator added

The following table gives the ratio of the deviation obtained with each variation to the maximum deviation allowed for the stock in routine tests.

Carcass Stock				
Variation	a	b	d	e
Deviation Obtained	4.1	4.1	1.7	2.3
Allowable Deviation				
Solid Tread Stock				
Variation	a	b	d	e
Deviation Obtained	3.9	1.1	2.9	1.8
Allowable Deviation				
Tread Stock				
Variation	a	b	d	e
Deviation Obtained	4.5	8.0	3.4	7.7
Allowable Deviation				

The response to serious variations in compound make-up is unmistakable.

Routine of the Test

A sample is taken from every milled batch and from the tubing machines and tread calenders at short intervals. Each is put through the routine of the test. If satisfactory, the operator files its identification card for laboratory inspection. If unsatisfactory, he sends the card back with a request for another sample, at the same time recording the name of the stock and its batch number on a form. The second sample follows the same routine as the first. If satisfactory, this is noted on the card and also on the form. If the second sample is unsatisfactory, the batch is ordered remilled for a new test. Should it then be satisfactory, the results are noted on the card and on the form; if unsatisfactory, the batch is held for laboratory test and disposal.

Forty minutes are allowed from the time the stock is milled or processed for the operator to make any requests concerning it. Should no word come during that time, it is understood that the stock is satisfactory and it is handled accordingly. The same time limit applies to the retests.

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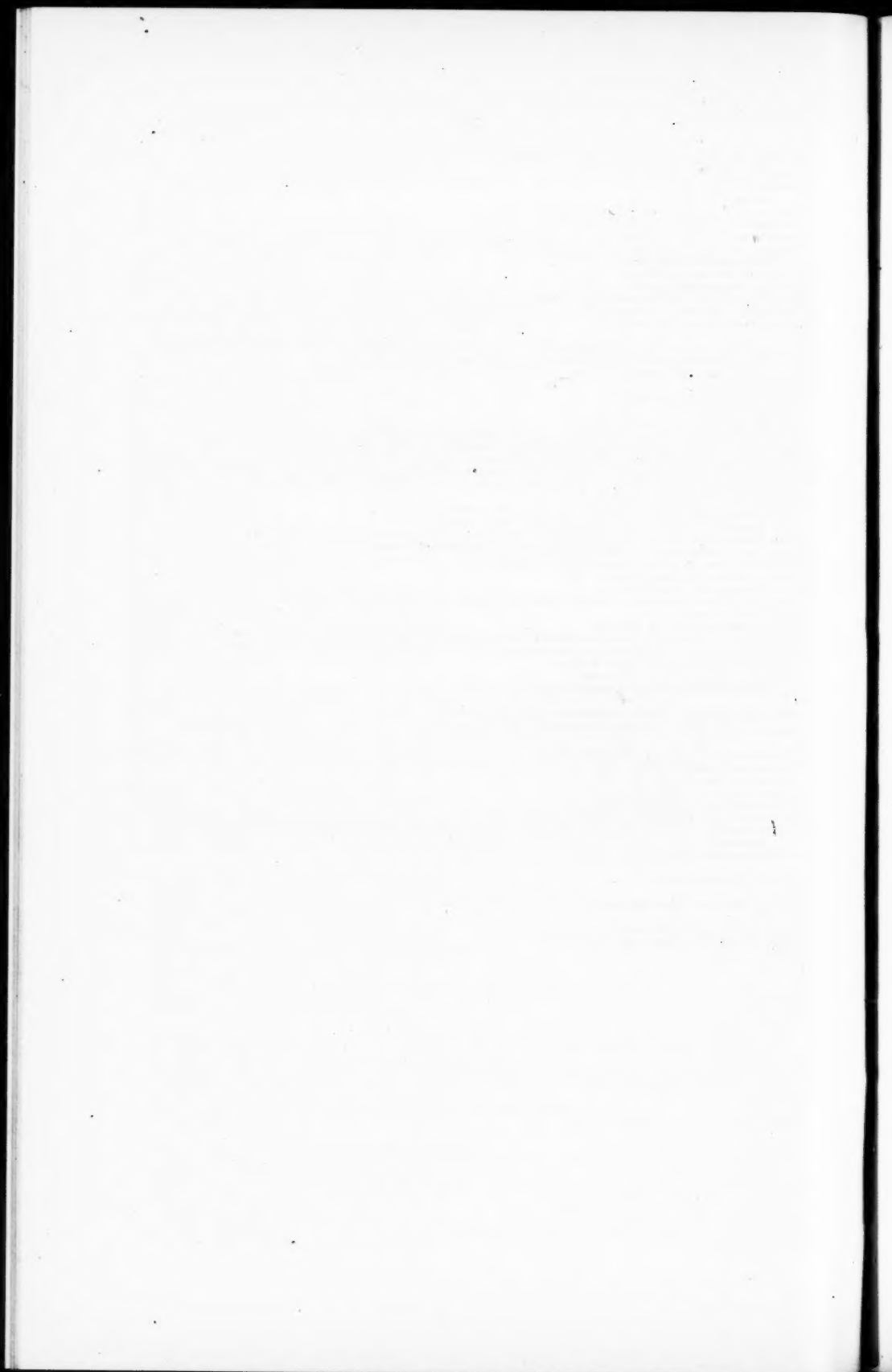
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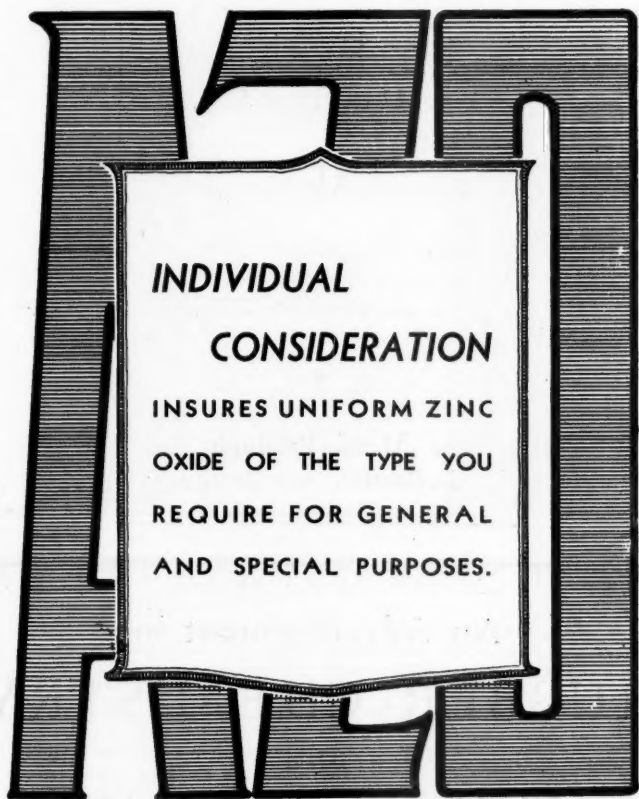
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Crylene.....	1.120	Resin	Hard rubber, mechanicals.
Hepteen Base....	0.937	Thin liquid	Friction and coat stocks, tubes, footwear, white sidewalls, sundries.
Hepteen.....	0.923	Thin liquid	20% the strength of Hepteen Base—same applications.
Trimene Base....	1.142	Thick liquid	Footwear, clothing, sheetings, sundries, mechanicals.
Trimene.....	1.027	Paste	Footwear, clothing, sheetings, sundries, mechanicals.
Semi Rapid			
DiEsterex N.....	1.24	Powder	Footwear, sheetings, tires, tubes, mechanicals.
Safex.....	1.57	Powder	Tires, footwear, mechanicals.
Rapid			
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Very Rapid			
CPB.....	1.17	Thin liquid	For room temperature vulcanization, or rapid vulcanizing at medium temperatures (175-200° F.) or very rapid curing at higher temperatures.
DBA.....	1.029	Thin liquid	
ZBX.....	1.561	Powder	

ANTI-OXIDANTS

Albasan.....	1.172	Flakes	Air cured goods, clothing, footwear, sheetings.
BLE.....	1.087	Liquid	Tires, tubes, soles, mechanicals, jar rings, footwear.
ODE.....	1.155	Powder	Rubber tiling, sundries, jar rings.
VGB.....	1.152	Resin	Wire, solid tires, mechanicals, rubber rolls.

SPECIAL PRODUCTS

Laurex.....	1.10	Pulverized	Special fatty acid and activator for general use.
Rubber Ink			In colors for decorating sundries, etc.
Rubber Labels			For trade marking rubber goods in two colors.
Sunproof.....	0.947	Pulverized	General use to prevent checking or cracking due to light.
Tonox.....	1.116	Solid	Activator, flexing improver. Bus tire carcass, high speed belt carcass, soles.

LATEX

Rubber in its natural form, as it comes from the tree. Carefully selected and stabilized.

LOTOL

Latex processed to meet specific requirements.

DISPERSITE

Aqueous dispersions of crude or reclaimed rubber, compounded to provide special characteristics.

RECLAIMED RUBBER

Standard grades for all purposes.

OTHER PRODUCTS OF THE NAUGATUCK CHEMICAL COMPANY

HEAVY CHEMICALS

A standard line of high quality.

VICTRON

A thermoplastic of unusual properties. Transparent and colorless, it is highly resistant to acids, inorganic bases and alcohols. Readily compounded with colors and fillers to provide any desired shade or properties. Furnished as a molding powder in solution, or as sheet, rod or tubing.

THE NAUGATUCK CHEMICAL COMPANY

1790 Broadway



New York City

High heat-conductivity *from chemically pure* Anaconda Zinc Oxide of uniformly fine particle size

Because of their exceptional fineness and unequalled chemical purity, Anaconda Zinc Oxides impart superior heat transmitting properties to rubber compounds.

In compounds used for bus tires, solid tires, motor mountings, bumper blocks...or wherever thick sections of rubber are subjected to repeated compression and distortion under load...plenty of good zinc oxide is necessary for the best performance.

We shall be pleased to discuss the effects of various zinc oxides in such compounds with you...and to furnish technical data on request.



ANACONDA ZINC OXIDE DEPT. of I. L. R. CO.

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Carload shipments from East Chicago and Akron
L. C. L. shipments from warehouses in principal cities

ANACONDA ZINC OXIDES

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ACCELERATORS
Ultra
Semi-Ultra
High Temperature

ANTI-OXIDANTS
Liquid and Powder.



The Rubber Service Laboratories Co. is *the* independent manufacturer of accelerators and anti-oxidants. It has no corporate affiliation with any rubber company.



The *only* company with a complete line. There is an R. S. L. accelerator or anti-oxidant for any type of cure, compound or process.



The *first* manufacturer to render a complimentary technical service. The keynote of the company when it was founded was *service*. It was incorporated into the name and has remained the primary object for over 10 years. Complete compounding laboratories are at your disposal.

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